6.0 DISCUSSION OF THE RESULTS

A number of limitations in the data collected during this project are presented in the previous chapters. These limitations aside, the data provide a view of the mechanisms involved in combustion, particularly as related to PCDD/PCDF formation. In this chapter the relationships between various parameters will be examined, the results will be compared to other test data, and possible explanations of the measured performance will be advanced.

Considerable study on PCDD/PCDF creation and destruction processes has been undertaken in the last few years. The papers presented at Dioxin 85 in Beyreuth, Germany provide insights into some of the basic mechanisms and are useful in interpreting the results of this test program. Unfortunately, these are not yet available in the open literature and citations are thus somewhat incomplete. Also, helpful in the interpretation are the results of test work completed after this series of tests, particularly the NITEP series including the P.E.I. work and the Quebec City APC tests. The original versions of Cooper (1985) including PCDD/-PCDF data were submitted for peer review and comment by interested parties. These comments are also helpful in trying to explain the results obtained. All this information and more was utilized in conducting the review in the following sections.

6.1 Operations Variability

During day two, two runs were made at each sampling point. While run C1 has been included in results presented to this point, the particulate loading data from that run will be excluded from further discussions due to the uncertainty of the data.

Monitoring of concentration levels at various points in the system utilizing modified Method 5 systems creates an average value for the test period. In the case of the Japanese study, the samples at A, B and C

reflect as close to real time averages as possible, i.e. residence times in the system are relatively short, however it can be argued that the same is not true for the D location. At D the fabric filter serves to dampen the system response by attenuating emissions and acting as a reversible sink for materials. This sink accumulates a layer of lime/-flyash over the 2-3 hour periods between cleaning and returns to a different state immediately after cleaning. The cleaning cycle time probably represents the minimum sampling period that should have been used however the interpretation must be made on the data available. Clearly, with the time delay introduced by the fabric filter it is necessary to consider not only the furnace operation during the test period but also for the period before testing started.
In considering the similarity of the two runs, furnace conditions, flow rates, temperatures and sampling data should be examined.

While limited, the operating data presented in Chapter 2 and the test data in Chapter 5 provide some indication of fuel feed and air flow rates during the test periods on day 2. MSW feed rate data show loading rates of 8.5, 5.7 and 6.1 T/hours for the three hours surrounding the first test; 2.3, 6.7 and 5.0 T/hours for the time around the second test. Average feed rates can thus be estimated as 6.8 and 4.7 T/hours respectively; this represents a decrease in throughput of 32%. Since combustion air supply is manually controlled, the excess air ratio would be expected to increase for the second test compared to the first, and it does go from 109 to 139% based upon gas analysis data at sample station A. Since the air is all supplied as underfire air, through the bed, increased particulate matter loads could have been anticipated for the second set of test data when compared to the first set of data.

Actual gas flow rates through the system decrease from the first to the second test (Figures 2.3-7 and 2.3-8 and Table 5.1-1) but this reflects the decrease in incinerator quench water more than any other single item.

Temperatures vary between runs, dropping the most in the furnace, the least at the fabric filter exit. The trend of reduced temperature on the second run is consistent. Most important though is the sidewall temperature data shown in Figure 2.3-1. Prior to test 1, furnace sidewall temperature dropped from 1454°F @ 2100 hrs to 1140°F at 2200 hrs and then rose to 1472°F at 2300 hrs, at which time testing commenced. Temperature was maintained at 1480 ±10°F until 0200 hrs when they started dropping to 1121°F at 0300 and 950°F at 0400 hrs when test 2 commenced. This test ran from 0400-0530 during which time sidewall temperature went from 950°F to 1508°F at 0500 and 1328°F at 0600 hrs. Clearly the first test was conducted under a more stable temperature regime than the second test. If the fabric filter does delay the output of pollutants from previous time periods, clearly there is more potential for the second sampling period to have been influenced by this than the first.

Temperatures are an indication of combustion efficiency and low temperatures are not considered compatible with good combustion. Martin (1984) in their comments on the test results note that, with the absence of overfire air, the gases from the grate would not mix well. The cold moisture-laden gases from the front-end of the grate would reach the quench zone without mixing with the hot combustion gases from the other parts of the grate. This cold air would act to quench part of the hot stream prematurely and reduce the completeness of the reaction. This process would limit the performance of the furnace under all operating conditions and give rise to higher levels of unburned materials and CO. Unfortunately, without a continuous emission monitor for CO or total hydrocarbons (THC), it is difficult to develop a thorough understanding of this effect.

Several observations are pertinent, however,

- short-term tests are inappropriate for the encountered operating conditions;

- combustion was likely poor, giving rise to higher levels of PCDD/PCDF production than the furnace would otherwise produce; and,
- continuous gas data would help with interpretation.

In the absence of such data, other measurement information should be reviewed.

6.2 Particulate Matter Sampling

An increase in particle loading was found from comparison of the first and second tests for locations A, B and D. This increase averaged 30-40%. While run 2C1 cannot be compared to 2C2 due to the leak detected during 2C1 sampling, the data for the other locations suggests that the assumed leakage rate for 2C1 is likely too high and that the correction factor should possibly be lowered. With the exception of 2C1, the data collected during the particulate/organic sampling runs would appear to be consistent with anticipated performance.

The system performance can also be reviewed by examining the back-half catch. With greater excess air temperatures in the furnace were lower, and the back-half catch increased. The greatest increase occurs after the fabric filter where the concentration increased by more than 14 times. Cooper (1985) suggests that this result may be caused by increases in the condensible matter trapped in the system. Further they suggest that a shift in the relative age of the material being sampled occurs, i.e. the fabric filter traps materials from earlier time periods and slowly releases them over the period of the sampling. Cooper (1985) suggests that condensible materials, generated during periods of lower furnace temperature, elute from the filter cake over time, until the filter is cleaned. The higher back-half catch levels are consistent with poorer combustion, a situation that would be anticipated based upon lower combustion temperatures and increased excess air levels prior to the test period.

Another possible explanation for the change in catch proportions at the fabric filter outlet may be a decrease in filter loading and a consequent increase in fines migration. Since the fabric filter has about the same efficiency as the filter on the sample train, fines passing through the fabric filter would only be trapped in the impingers. Loading was reduced for test two - due to lower APC Quench Reactor feed rates during the low temperature period. Decreased stack gas moistures accompany this situation and may influence the agglomeration of the lime, flyash and Tesisorb in the system.

Bag cleaning schedules could also influence the distribution. Hindy (1986) shows the influence of fabric filter cleaning on emission levels. During the period immediately following cleaning, emissions are 3 to 4 times higher than recorded at the end of the filtering cycle. Should the filter have been cleaned during the sampling period, higher emissions would have resulted and these would have contained the fines from the previous period.

6.3 Particle Sizing Data

6.3.1 Particulate Loading Rates

The particle sizing data can be compared to the front half catch for the particulate sampling runs thereby providing an indication of protential changes in performance between the two days. Such a comparison is provided in Table 6.3-1. Some differences are evident in this data.

Sampling times for particle sizing with the multiple cyclone at locations B and C were between 30 and 45 minutes, somewhat shorter than times for particulate train sampling. The particle sizing run at location D took eight hours, considerably longer than the other runs. Since fabric filter cleaning has been shown to influence emissions (Hindy, 1986) this could account for some of the variability.

TABLE 6.3-1

Comparative Grain Loading (g/Nm^3 @ 12% CO_2)
Particulate Runs versus Particle Sizing Runs

Test Location	Particulate Front Half Loading	Particle Size Loading
A	4.04, 5.40	NA
B	4.49, 5.95	5.7, 7.6
C	9.61	5.8, 11.4
D	0.03, 0.04	0.006

Another explanation is provided when one examines the representativeness of the samples based upon the relationship of the sampling location to disturbances before and after it. This issue is particularly critical at locations B and C. Location D should be satisfactory.

Rigo (1984) in his review of this work suggested that the overall distribution of various size fractions will be adequately represented by a near centerline sampling location, provided the material is fine. He suggests that for particles of aerodynamic diameter 10 μm and smaller the tendency is that they follow the gas stream. Rigo cites the work of S.L. Soo who demonstrated that large particles are subject to gravitational effects on horizontal ducts whereas electrostatic effects force the fines to the top. Rigo suggests that in a bend the fines would be forced inwards with the large particles moving to the outside.

This argument can be used to develop an hypothesis to explain the observed variations between full traverse grain loadings and single point values, even allowing for the inherent variability in the data. The averaging effects of full traverse sampling could reduce the concentration values from those found at single points.

More lime was being added at the APC quench reactor on Day 3 and this would also have the effect of increasing the apparent loading at B and C when measured by particle sizing methods. Within these limits, the data for the two days appear consistent at points B and C.

Point D values show a wider discrepancy between Modified Method 5 and particle sizing grain loadings, however several issues must be considered:

- the fine fraction data for the multiple cyclones at D is an estimate based upon Anderson data,

- the standard deviation on six Method 5 results at D was 75% of the average value suggesting that the data have significant variability,
- small errors in total particulate weights per stage could produce significant variations in grain loadings; and,
- fine particulate can coat the walls of the cyclone system and not be totally removed during recovery procedures.

Any combination of these explanations could give rise to the grain loading results obtained from the particle sizing run at point D.

6.3.2 Particulate Size Distribution

Table 5.5-3 shows that each multiple cyclone sample provides roughly similar "cut" sizes. The D_{50} values, the size at which 50% of the sample size was larger and 50% smaller than the given D_{50}, vary from 2.2 to 2.9 μm for the smaller cyclone and 11.0 to 12.9 μm for the large size. Analysis of this distribution information is limited due to the burnt filter from the multi-cyclone at location D. Also limiting the analysis is the lack of sufficient stages in the separation to confidently predict a mass mean aerodynamic diameter.

Andersen data for the same test day is provided in Cooper (1985). This data is plotted in Figure 6.3-1, and shows that the mass mean aerodynamic diameter (MMAD) for the fabric filter outlet is approximately 5 μm. Mean mass diameter values for other points in the system are 12 μm at C and 70 μm at B. These latter values would appear reasonable given the process, however, the value at D appears to be high when compared to other data.

SYSAV (1983) data shows MMAD values ranging from 2.1 to 3.1 μm depending upon loading in the system. Twenty percent excess lime [70 kg/hr. (154 lb./hr.)] showed 2.8-3.1 μm diameters; at 31% excess (100 kg/hr. or 220 lb./hr.) the value was 2.7 and at 65% excess lime (210 kg/hr.,

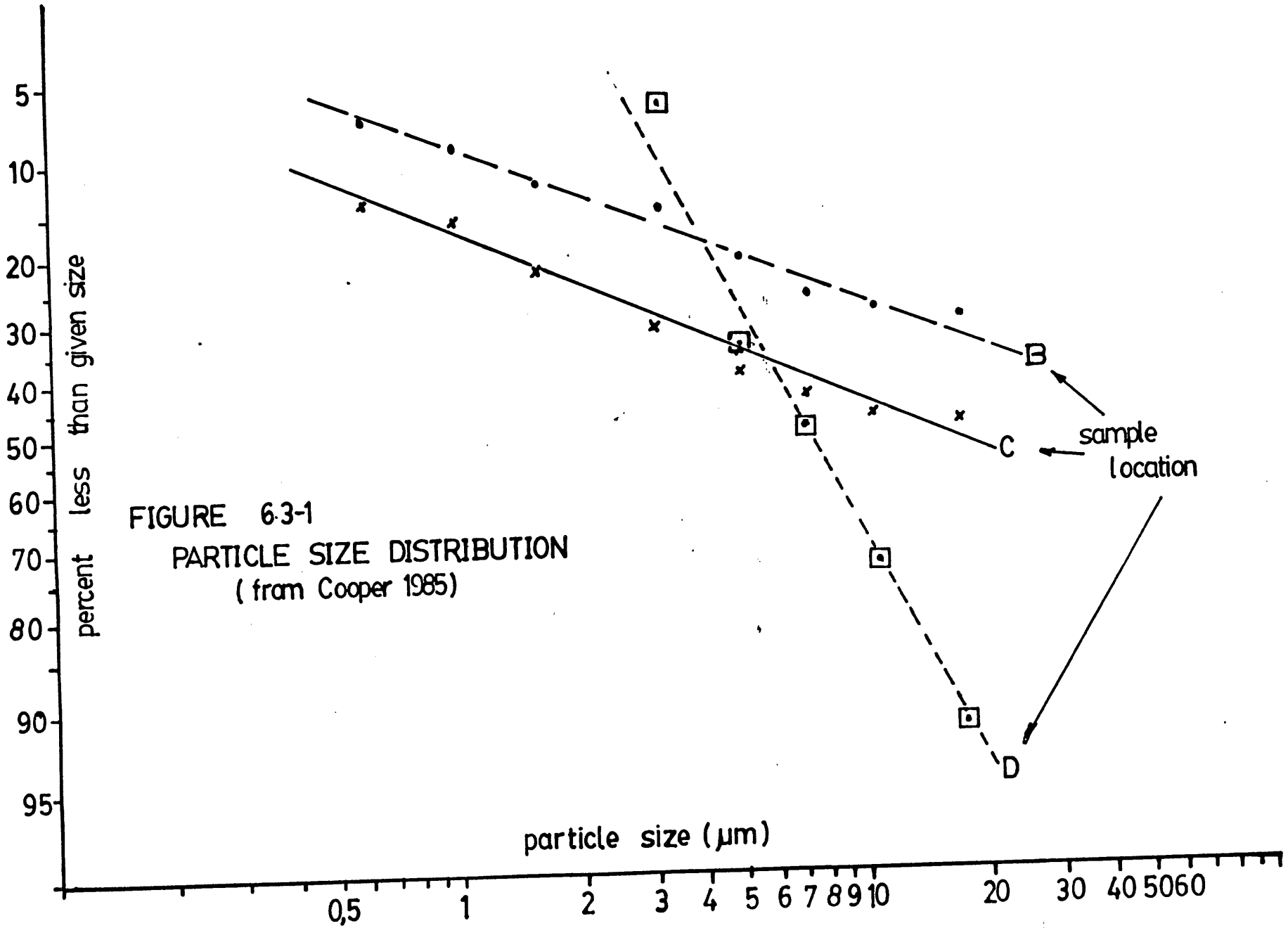


FIGURE 6.3-1
PARTICLE SIZE DISTRIBUTION
(from Cooper 1985)

462 lb/hr.) the MMAD was 2.1 μm. The fact that the fabric filter outlet MMAD is nearly twice as high for the Japanese test data suggests that some deficiency exists either in sampling or in system operation. Likely explanations include:

- poor sample recovery technique - weights were not correct;
- fabric filter leakage was occurring; or
- insufficient sampling time was used.

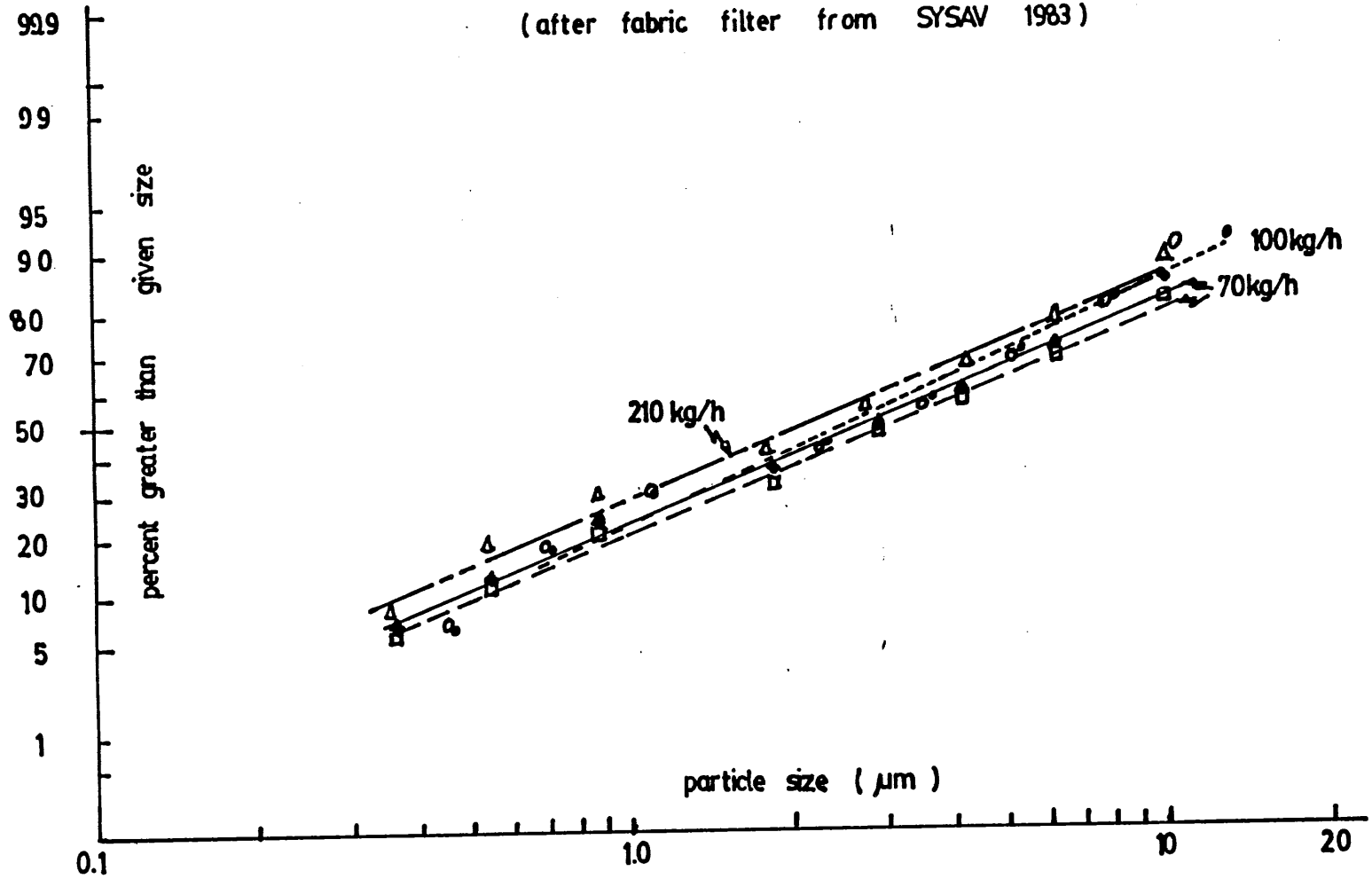
As a comparison the SYSAV data is offered in Figure 6.3-2.

Fabric filter leakage due to pinholes is not suspected since the outlet distribution is significantly different from that at location C (Dennis et al., 1977).

The absence of any material trapped on the last two stages of the Anderson impactor and the filter indicates insufficient sample time given the anticipated grain loading in the fabric filter outlet. Data in Cooper (1985) indicates that less than 8 mg total were recovered from the Andersen sampler at location D. Most methods suggest 50 mg of material is necessary to ensure that a representative sample is collected. The actual flow rate through the sampler and the eight hour sampling time should have been sufficient for a 0.003 gr/ACF stack loading. This value is less than the flue gas grain loadings recorded during one and day two testing with the exception of 1D2 which was approximately 0.002 gr/ACF, however, the front half loadings for most runs were below this value. This again points to the release of considerable amounts of extremely fine material from the fabric filter. This portion could amount to 20 to 50% of the total material escaping the fabric filter.

Unfortunately cascade impactors will not adequately sample such fine materials and the fabric filter outlet size distributions are likely biased high because of this ineffectiveness.

FIGURE 6.3-2 PARTICLE SIZE DISTRIBUTION
(after fabric filter from SYSAV 1983)



Even with these limitations, both the particulate matter sampling results and the particle sizing data provide information on the operation of the fabric filter.

6.4 Fabric Filter Performance

6.4.1 Comparison to Other Systems

In 21 tests conducted on a fabric filter following a dry reactor in Sweden (SYSAV, 1983) a marked relationship between lime feed rates and exit dust concentration was found. Increasing the feed rate by 50% lowered the emission level by 50%. A further increase to three times the initial rate resulted in an exit dust concentration that was 11% of the initial value. This data clearly illustrates a relationship between bag loading and control efficiency.

Recent tests by Environment Canada on a pilot scale dry reactor/fabric filter showed fabric filter outlet concentrations of 2 mg/Nm^3 (NITEP, 1986). These values were measured as total catch in the impingers and washings since the filter was not used in the sampling train. NITEP (1986) reports other data on similar systems indicating typical emissions to be in the 4-40 mg/Nm^3 range. Data cited includes Kempten, Germany and Geiselballach, Germany with results of 4-5 mg/Nm^3 and a hazardous waste facility in Finland with levels of 10-20 mg/Nm^3.

The short duration of most of the tests in the Japanese series may contribute to more data scatter, particularly since lime slurry feed rates to the APC quench reactor are controlled by furnace temperature and can fluctuate. Total concentration data for this test series at the fabric filter outlet ranges from 12 to 280 mg/Nm^3 at the actual CO_2 concentration (20 to 560 mg/Nm^3 @ 12% CO_2). This range is higher than much of the reported data, and suggests performance deficiencies. In examining this performance the relationship of loading to removal efficiency was reviewed.

The combination of Tesisorb and lime being fed to the dry venturi can be estimated from a mass balance for run 2B2/2C2. While the times for these runs were slightly different, the average value should be a good approximation. This number suggests that 130 lb. (59.3 kg) of material was added per hour; the plant data in Chapter 2 lists 192 lb. (87.3 kg) as being added per hour. The total load to the fabric filter is 140.5 kg/hr. suggesting that, by comparison to the SYSAV data, a good removal efficiency should be achieved. For the 2D2 run the removal efficiency is only 94.5%. On day one Cooper (1985) shows the removal efficiencies to average 98.8%. Neither of these levels is near the anticipated removal efficiencies for fabric filters, particularly considering the low air to cloth ratio quoted by Cooper (1.9 ft^3/ft^2). Carr and Smith (1984) suggest that a well maintained fabric filter, operating on power plant flue gases, should achieve extremely high large and fine particle collection efficiencies. Overall reverse-gas cleaned units will achieve mass collection efficiencies of better than 99.99%.

The inability of the tested system to meet these levels indicates that:

- the bags may be being cleaned too often;
- the bags may be too new to have achieved an equilibrium condition; or,
- the bags may be damaged.

A review of the particle sizing data in Figure 6.3-1 suggests that bag damage is not a likely cause of the performance deficiency since the particle size distribution shifts noticeably between points C & D. Dennis et al. (1977) suggest that if penetration is due to pinholes the outlet size/mass distribution will be the same as the inlet distribution.

The review of fabric filters prepared by EPRI (Carr and Smith, 1984) states that the majority of emissions from a baghouse occur within a few minutes of cleaning and thus total emissions are directly proportional to

cleaning frequency for any application. Detailed measurements show that these emissions contain fine particles that penetrate the filter media and agglomerates that bleed through the fabric and break loose during cleaning. Similar to the cleaning phenomenon, Carr and Smith (1984) indicate that experience with full scale fabric filter installations has shown that bag performance improves over the first six months of operational life, thereafter remaining fairly constant.

If the filters do achieve this equilibrium performance level, Carr and Smith (1984) present an empirical equation to define tube sheet pressure drop:

$$\Delta P = 3 \text{ (Air to Cloth Ratio)} \pm 20\%$$

For this application, this equation would provide a ΔP from 4.44-6.84 inches H_2O. Adding 2 inches H_2O for duct work implies that the ΔP across the baghouse should range from 6.44 to 8.84 inches. The operating data, although limited, shows values from 5.1-5.5 inches H_2O for 2D1 and 4.7 to 5.1 inches H_2O for 2D2. These are below the predicted values and may provide some evidence of the possible cause of emission rates being higher than anticipated. Lower pressure drops are associated with newly cleaned bag filters and higher emissions. During the particle sizing run on day 3 the ΔP was 6.7-9.4 inches H_2O, again providing more corroboration of fabric filter performance versus pressure drop, since the front half catch suggests that better emission values were obtained on that day.

Also, supporting the theory of of fine particle release from the fabric filter is the back-half catch data. As a percentage of the total catch these vary from 50% on 2D1 which has one of the lowest emission rates to 91% on 2D2 the highest emission rate.

6.4.2 Summary of Operational Data for Fabric Filter

The operational variation of the incinerator on day two was discussed earlier. These conditions likely gave rise to variations in the flue gas quality both before and after the APC system. Flow rates dropped at all sampling locations and particulate matter concentrations at A and B rose by approximately 40%. The increase in particulate matter concentrations was most pronounced after the fabric filter where the concentration increased by a factor of 10.

Performance of the fabric filter, as assessed from the second run on day two (94.9% removal), and the data reported by Cooper (1985) was:

- 1C1 - 1D1 - 98.6%
- 1C2 - 1D2 - 99.8%
- 1C3 - 1D3 - 97.9%

These figures suggest that the fabric filter was not operating at peak efficiency most of the time, since normal removal efficiencies should be greater than 99.9%.

Review of the limited particle sizing data at the fabric filter discharge indicates the possible emission of large quantities of <0.5 μm material. This material cannot be measured by in-stack particle sizing equipment of the type employed for this study. However, it would be trapped in the impingers after the filter on particle sizing, EPA 5 and MM5 trains. High back-half catches are recorded for several tests, indicating the presence of fine materials.

A review of the available data reinforces the hypothesis that the fabric filter was not operating at its optimal performance level. New filters can take up to six months to achieve stable removal performance (Carr and Smith, 1984). If the filters were punctured or broken, the particle size distribution at the fabric filter outlet should approximate that at the

inlet. This was not the case and thus the "green" bag explanation is the most appropriate. This is further reinforced by the overall low ΔP values observed for the fabric filter system particularly during periods of high emission values. These were significantly below values suggested by EPRI.

The performance of the fabric filter would be anticipated to influence not only particulate matter emission rates but also those of various trace metal and trace organic compounds in the gases.

6.5 PCDD/PCDF Measurements

6.5.1 Emission Levels

Two emission levels are available for the Japanese plant, the uncontrolled levels of PCDDs/PCDFs at sample location A and the controlled value at the fabric filter discharge. These values will be compared to literature data in this section of the report. Only two test values are available for comparison to other data; 2A1 and 2A2 define uncontrolled incinerator emissions and 2D1 and 2D2 define controlled emissions.

6.5.1.1 Uncontrolled Emissions

The values for uncontrolled emission levels are:

- 207 and 392 ng/Nm^3 @ 12% CO_2 PCDDs; and,
- 475 and 4041 ng/Nm^3 @ 12% CO_2 PCDFs.

There would appear to be no significant difference in the PCDD values, (applying ±%RSD to the values shows an overlapping range). The PCDF data appear to be significantly different. Even though no %RSD values are available for PCDF surrogates, the more than 8 times greater values for 2A2 shows a marked change in concentration.

Chapter 4 discusses surrogate recovery data and shows up to 45% relative standard deviation in the recovery values. These values were recorded for the impinger contents which had the majority of the PCDD/PCDF catch. Comparison of data between runs should consider this variability. For the purposes of the discussion that follows, the author has assumed that significant differences can only be said to occur if the values differ by greater than a factor of two (2).

In support of this approach, Karasek and Hutzinger (1986) note that Crummett reported that 19 of the isomers with a 2,3,7,8 substitution could be determined with acceptable confidence and, that 1 ng/g (10 ppb) analyses can be consistently achieved with a standard deviation of ±100%. Recoveries from sample cleanup of 50-125% are achievable 50-95% of the time. This data emphasizes the need for some latitude in data interpretation.

Only limited data are available for comparison to these uncontrolled results. The Japanese incinerator is not equipped with heat recovery and thus has a different cooling regime from most plants studied in the literature. Beychok (1986) identifies several data sets for PCDD/PCDF emissions from MSW incinerators without heat recovery. All the units have some control devices built into the system and the results typically include the effects of these systems, as only exit concentrations are measured. Table 6.5-1 summarizes the available data.

Several observations can be made from this data and comments in the references. DeFre (1985), as cited in Karasek and Hutzinger (1986), states that:

- measured PCDD/PCDF emissions did not have a dependence on operating temperatures in the 800-1050°C (1470-1920°F) range;
- measured PCDD/PCDF emissions had little dependence on the source of the waste; and,

TABLE 6.5-1

Comparison of PCDD/PCDF Emission Concentrations from MSW Incinerators
(ng/Nm^3 @ 12 % CO_2)
(from Beychok, 1986)

Plant	# of Tests	Comubstion Temperature (°F)	Control Device	PCDD	PCDF	Ref.
Japanese	1	1600-1625	(Water Quench	207	475	
(inlet to APC)	1	1085-1640	to 680°F)	392	4041	
PEI (boiler Inlet)	9	1650-2010	None	5	14	(CSC, 1985)
Toronto	3	1600	Water Quench ESP	3800	3700	(Ozvacic, 1985)
Zaanstad, Holland	8	1670	ESP	2510	2880	(Beychok, 1986)
Harelbeke, Belgium	21	1500-1900	ESP	7640	8150	(DeFre, 1985)
Brasschat, Belgium	32	1500-1900	ESP	1620	6000	(DeFre, 1985)

- measured PCDD/PCDF emissions had no dependence on possible PVC precursors in the waste.

Beychok (1986) shows a substantial variation in excess air between the two DeFre results, 456% at Harelbeke and 268% at Brasschat. If one can accept DeFre's findings that there was no dependence on the waste, there appears to be a direct relationship between excess air and total PCDD/-PCDF levels. A similar situation appears to exist for the Japanese data that is the subject of this report, but caution must be exercised when drawing the conclusion since the operating temperatures are generally below those reported by DeFre. The temperature dependence of PCDD/PCDF emissions has been shown to be strong in some data [Hampton EFW data as reported by Hasselriis (1985)].

One additional piece of data should be introduced at this time: the APC system inlet conditions for Quebec City (NITEP, 1986). In a test similar to the Japanese work, a pilot scale wet and/or dry reactor and fabric filter system was tested on a Von Roll unit at Quebec City, Canada in the summer of 1985. The plant dates back to the early 1970's. This unit is a water wall furnace and the gas temperature averaged 510°F at the APC inlet. Tests were performed on a slip stream of the gases from the No. 3 unit.

The two APC systems are very similar. The Quebec APC system consisted of:

- a quench reactor for water or lime slurry injection;
- a dry reactor for lime addition; and,
- a fabric filter with Teflon coated bags.

Comparing this to the Japanese system the only differences are:

- lower system inlet temperatures at Quebec since the system was after the water wall furnace;

- the Quebec City system had the flexibility to introduce water or lime slurry for quenching; and,
- the system did not use a filter aid such as Tesisorb.

Values of PCDD/PCDF at the Quebec City APC inlet, averaged for the 12 test runs, were:

PCDD - 1120 ng/Nm^3 @ 8% O_2
PCDF - 720 ng/Nm^3 @ 8% O_2

Unfortunately CO_2 readings were not available from continuous analyzers at this site and detailed data are not yet available to the public, therefore these values cannot be expressed in the standard format used in this report. These values are within a factor of 3 for PCDDs and within the PCDF range reported for the Japanese study. Interestingly the overall PCDD:PCDF ratio is significantly different at Quebec City, there are more PCDDs than PCDFs.

Although not strictly comparable, the PEI data (CSC, 1985) provides another comparison to the Japanese location A data. Average stack concentrations of PCDD/PCDF after the boiler (180°C, 356°F) were:

- PCDD - 109 ng/Nm^3 @ 12% CO_2,
- PCDF - 134 ng/Nm^3 @ 12% CO_2.

The PEI facility has no APC controls and these values represent uncontrolled emissions. As with the Quebec City data the PCDD:PCDF ratio at PEI is significantly different from the Japanese experience. Comparison of the total PCDD/PCDF concentrations entering the APC system in the Japanese plant versus other data does not provide a great deal of insight into the reasons for the variations recorded between the two Japanese tests. Much of the literature data is averaged and the averaging process hides variations and makes it difficult to draw inferences.

Given the values in Table 6.5-1, the uncontrolled Japanese results, while variable, are in the range of the lower numbers reported by others for systems without boilers.

6.5.1.2 Variations Within the APC System

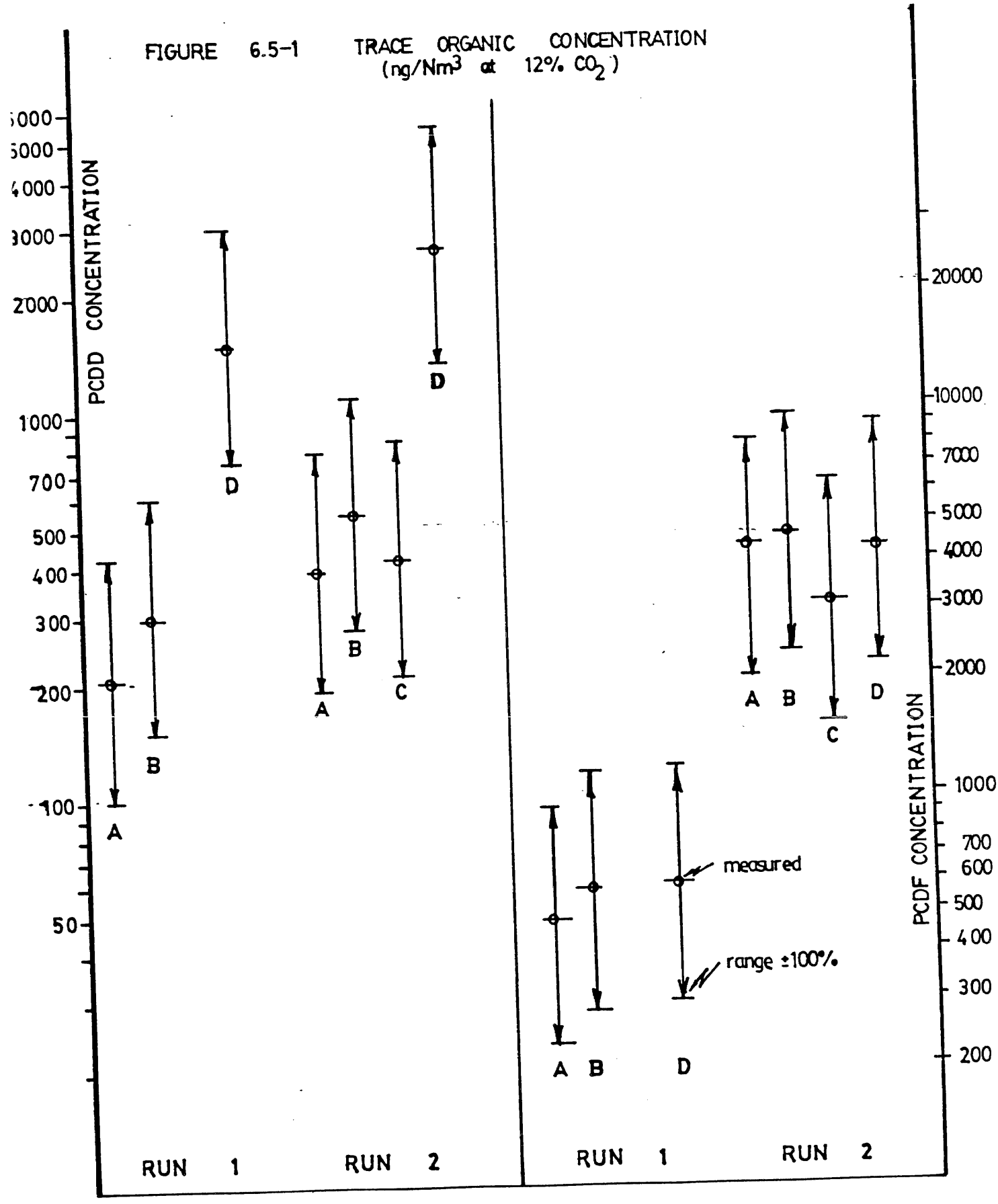
Figure 6.5-1 is a plot of the total PCDDDs/PCDFs found at each location for each test. Not included here is the particle sizing data, as that information only provides values of concentrations in the relatively large size fraction material, and is of only limited value due to the detection limits of the method.

Run to run variation can be examined by comparing concentrations of PCDDs and PCDFs found at the various sampling stations. Several observations can be made from the data in Figure 6.5-1:

- while overall PCDD results are similar for the two runs, PCDF results are markedly different, (the second test produced values 6 to 8 times greater for PCDFs);
- PCDD values after the fabric filter are significantly higher than levels before the filter for both tests, similar results are not observed for PCDFs;
- the ratio of PCDDs to PCDFs is similar for both tests for locations A and B but markedly different for D. PCDDs contribute 31-34% to the total values at A and B but 71% at D for test 1; PCDDs account for 8-12% of the total for test 2 at A, B and C, whereas 38% of the total at D is composed of PCDD.

Unfortunately, only two data points exist for the Japanese tests and any correlation is tenuous. However, one observation is readily apparent, the fabric filter outlet values do not compare well with the inlet and P quench reactor exit values. This again supports the contention that the fabric filter outlet values may be subject to other influences.

FIGURE 6.5-1 TRACE ORGANIC CONCENTRATION
(ng/Nm^3 at 12% CO_2)



These results suggests that a review of the ratio of PCDD to PCDF may be appropriate. Figure 6.5-2 presents data from the Japanese test set and Figure 6.5-3 data from other tests. Comparisons can be made to both the NITE PEI (Concord, 1985) and NITEP QC APC (NITEP, 1986) data. These latter two data sets are shown in Table 6.5-2.

The majority of the data on the plot are from the Quebec City APC System test series (NITEP, 1986).

Plotting PCDD vs PCDF for the Japanese data shows all values for locations A, B, and C to be well correlated. The disparity in the D location values is even more evident on this plot as these values are shifted to the right and have a significantly different slope to that of the other data. Table 5.4-3 shows the combined ash and fabric filter ash samples to have a distribution closer to the 2D1 distribution than to any others. This is additional proof of the validity of the apparently anomalous fabric filter exit data. The ratios of PCDD:PCDF is less than 1 for all but the 2D1 run.

As with the Japanese data for the inlet and quench reactor discharge, the Quebec City inlet and Quebec City fabric filter inlet values correspond very well. The fabric filter outlet values for Quebec City range from 0 to 8 ng/Nm^3 @ 8% O_2 for PCDD and from 0-3 ng/Nm^3 @ 8% O_2 for PCDF. The PCDD:PCDF ratio for the outlet is consistently 1 or greater, as are the other values.

The NITEP PEI data reflects stack conditions. Within the level of accuracy for the data the ratio of PCDD:PCDF is less than 1; except for the low temperature case where excess air levels are much higher and more PCDDs than PCDFs are present. The PEI data for runs 2 to 10 more closely resemble the patterns of the Japanese data than those of the Quebec City data. The major differences between the systems is the excess air levels. With the absence of overfire air, due to operating

FIGURE 6.5-2 PCDF VS PCDD

FOR JAPANESE TEST

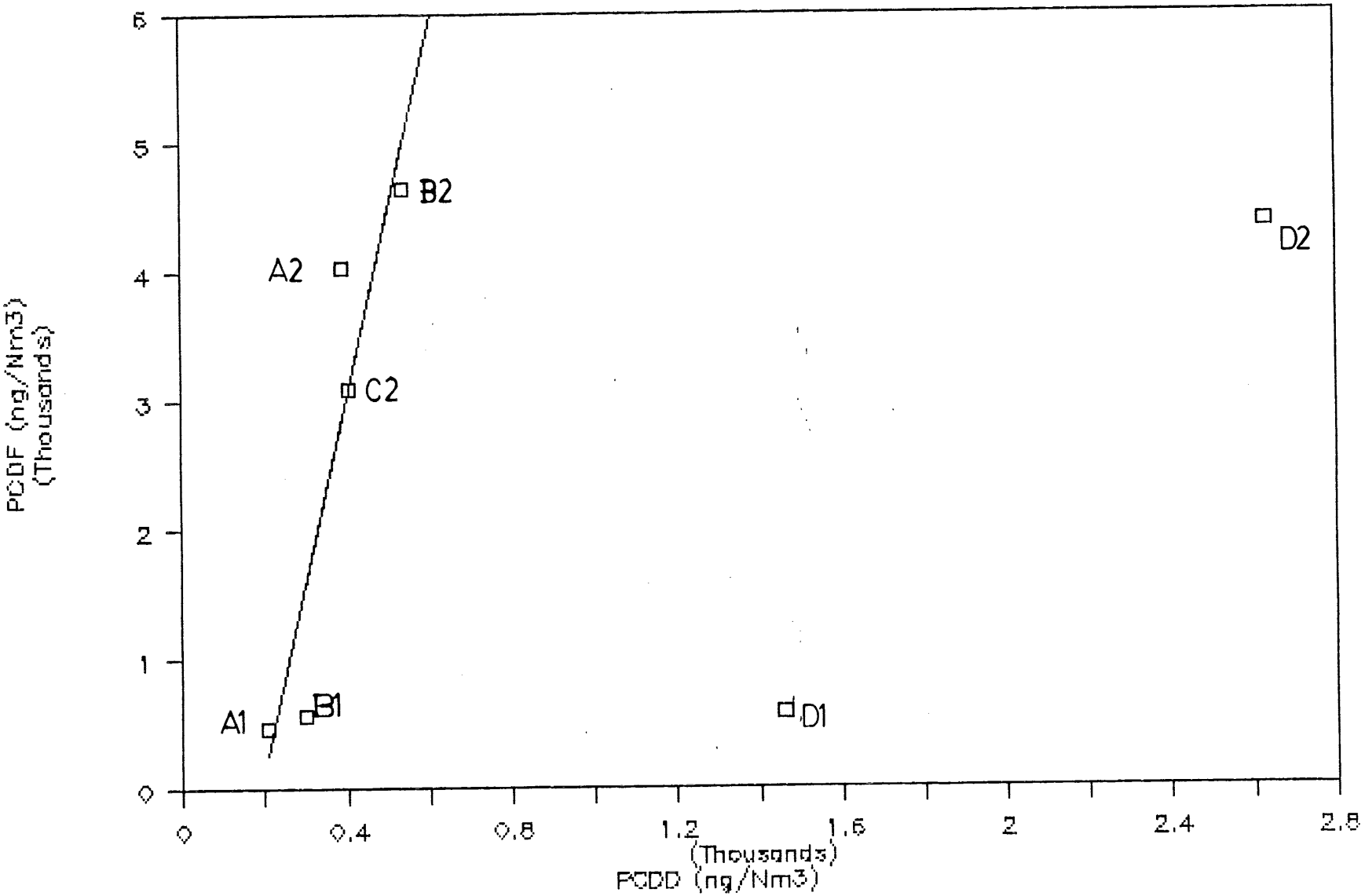
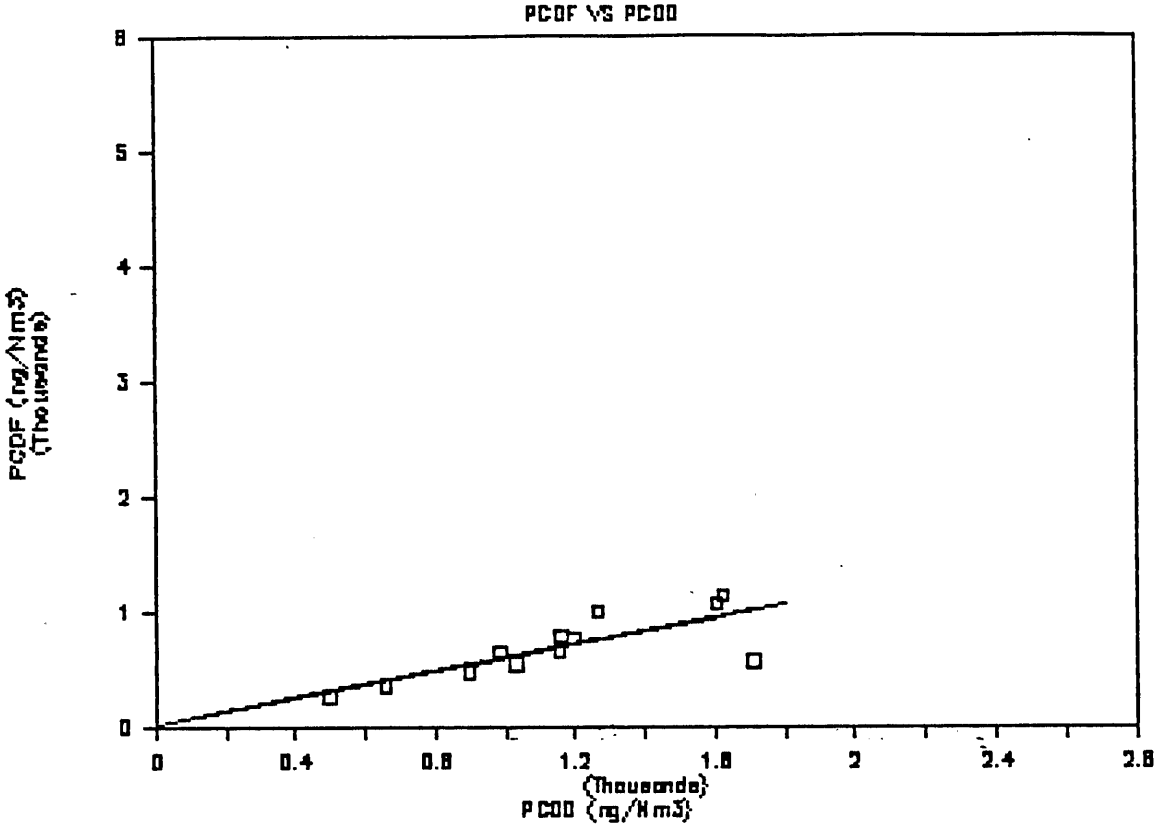


FIGURE 6.5—3a QUEBEC CITY APC



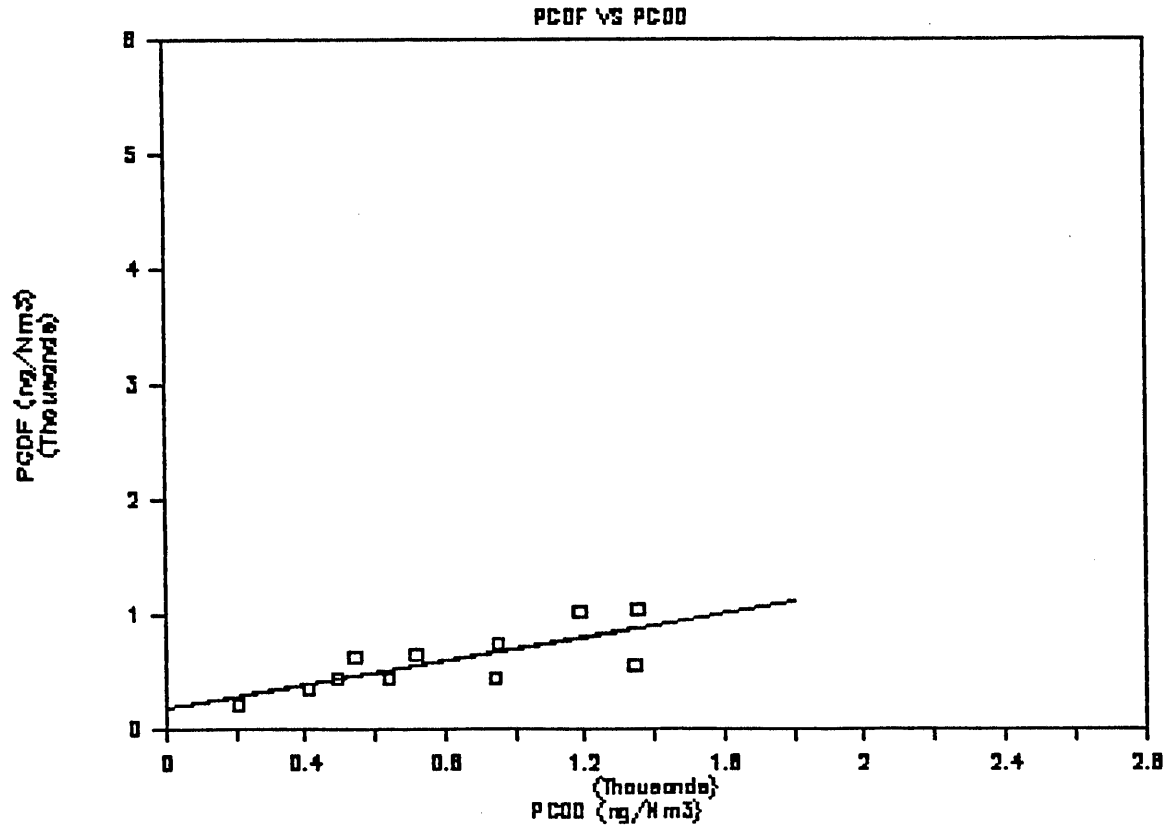
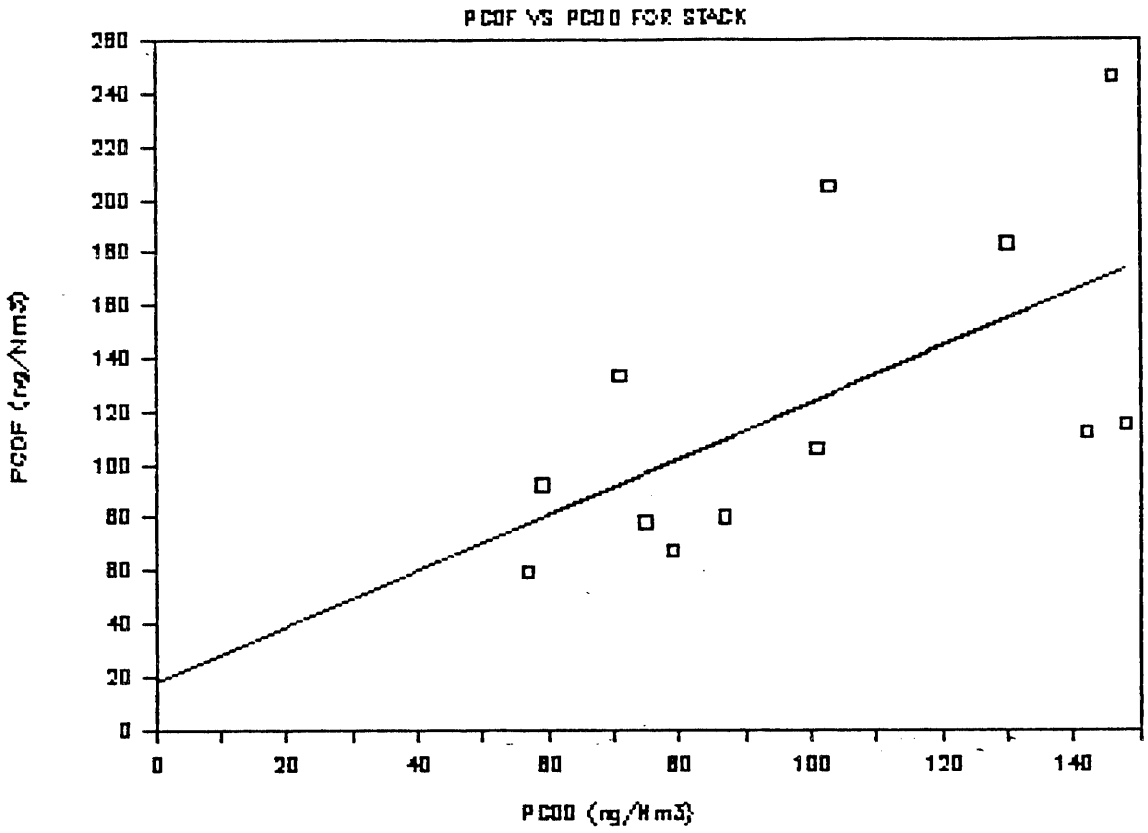


FIGURE 6.5—3b PEI TESTS



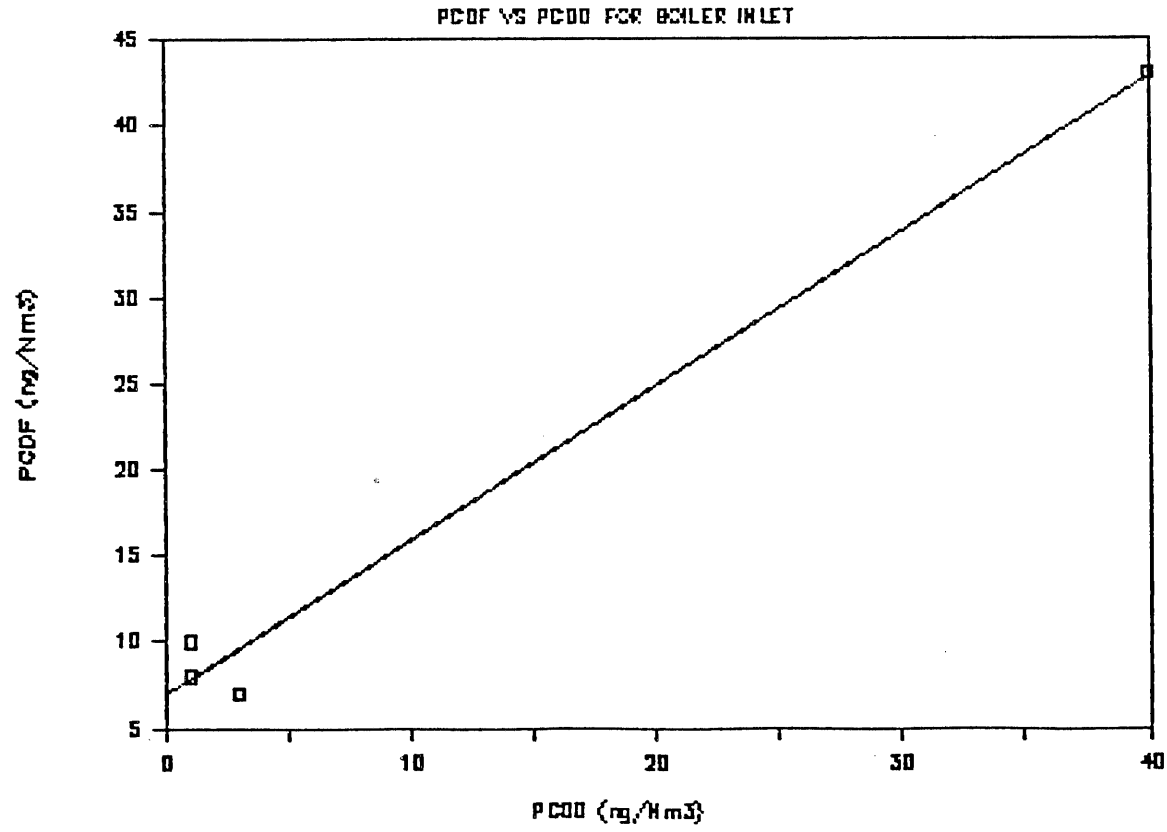


TABLE 6.5-2

Comparison of Total PCDD and PCDF Concentrations at Various Sites (ng/Nm^3 corrected for excess air)

Site	# of Tests	PCDD	PCDF
Japanese	2A1	207	475
	2A2	392	4041
	2B1	299	571
	2B2	541	4653
	2C2	408	3096
	2D1	1461	592
	2D2	2630	4373
PEI Stack	PT2	146	246
Ref. (CSC, 1985)	PT3	101	106
	PT4	75	78
	PT5	87	80
	PT6	103	205
	PT7	130	183
	PT8	57	59
	PT9	71	133
	PT10	59	92
	PT11	148	115
	PT12	142	112
	PT13	79	67
Quebec City	PT01	1709	564
APC Tests Inlet	PT03	1194	756
Ref. (D. Hay, 1986)	PT04	1624	1130
	PT05	1155	658
	PT06	898	470
	PT07	1158	787
	PT08	1032	537
	PT09	1603	1070
	PT10	986	637
	PT11	1264	1001
	PT12	659	353
	PT13	498	255
Quebec City	PT03	642	433
APC Tests Midpoint	PT04	491	439
Ref. (D. Hay, 1986)	PT05	1345	550
	PT06	941	427
	PT07	952	744
	PT08	718	636
	PT09	1354	1045
	PT10	1189	1015
	PT11	544	627
	PT12	410	340
	PT13	208	203

procedures at the Japanese facility, the system would operate at lower excess air levels than the Quebec City system. PEI is a controlled air incinerator with excess air more closely controlled. Hasselriis (1985) notes that more PCDFs form in systems with low O_2 levels and conversely more PCDDs form with high O_2 levels. This hypothesis is opposite to the effect noted for 2D1 versus 2D2 and again suggests that the fabric filter slows system response and actually reflects earlier system performance.

It is perhaps more important to note that within the Quebec City system the ratio of PCDD:PCDF does not change drastically between inlet and midpoint. The lack of measurable quantities makes it difficult to carry this conclusion to the fabric filter exit. In the Japanese case it is clearly evident that the fabric filter exit data is different from that collected on the other five tests. Little if any difference exists between data from points A, B and C on the two runs. This pattern supports the previous argument that the filter delays the emissions by a finite time period and thus emissions at time t represent operating conditions at t-u, some time earlier.

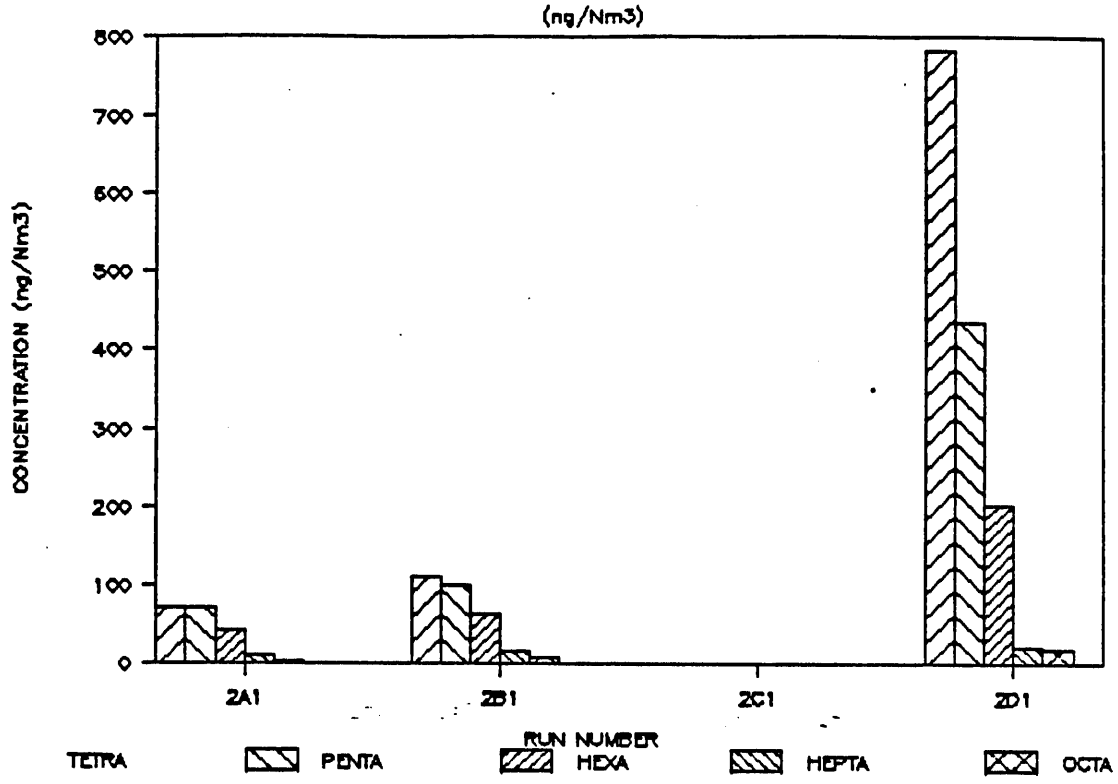
The distribution of homologues of PCDDs and PCDFs can also provide important information on system operation. Plots of these data are provided in Figures 6.5-4 and 6.5-5.

Several observations are immediately apparent from these plots:

- the concentration is maximum for the tetra homologues, with the exception of PCDDs for 2D2 where penta homologues dominate;
- the PCDD concentration at D is considerable higher for all homologues; and,
- within the range of accuracy of the analysis TCDD/TCDF homologues dominate in the ash systems and the particle size data.

The first observation is unusual (Ozvacic et al., 1985) but was also noted in the SWARU (Hamilton, Canada) tests. Ozvacic et al. advance the

FIGURE 6.5-4 PCDD HOMOLOGUE DISTRIBUTION



PCDD HOMOLOGUE DISTRIBUTION

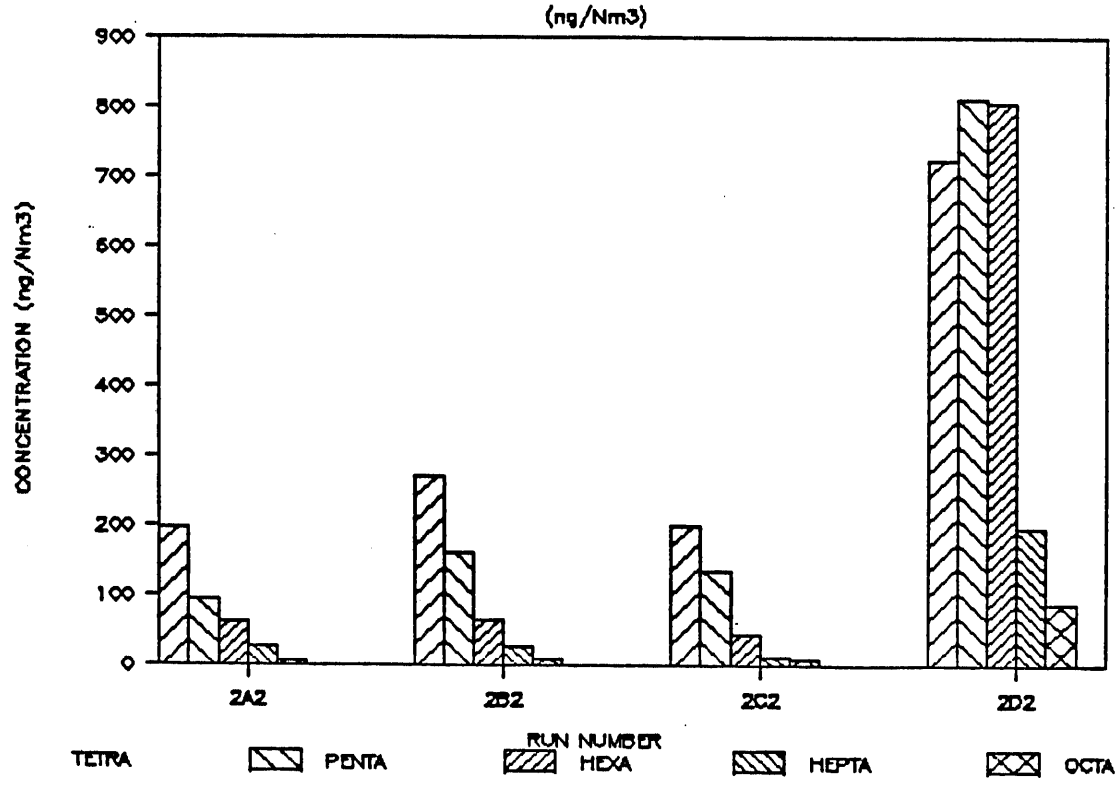
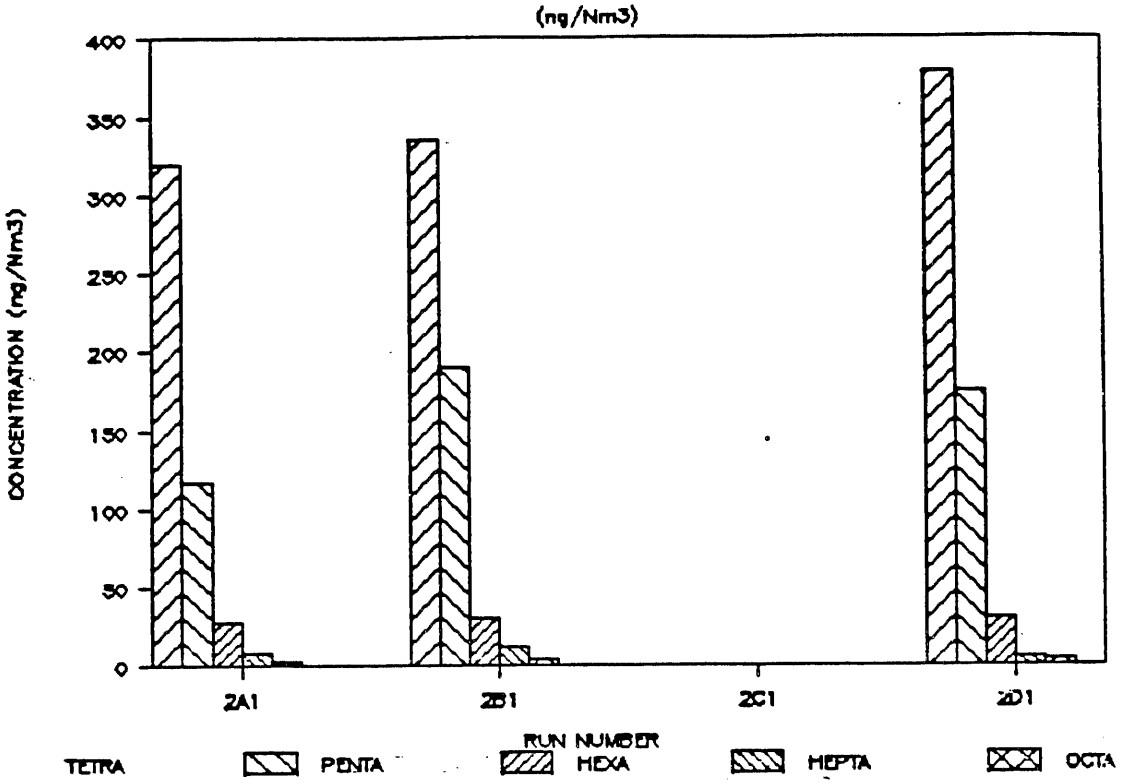
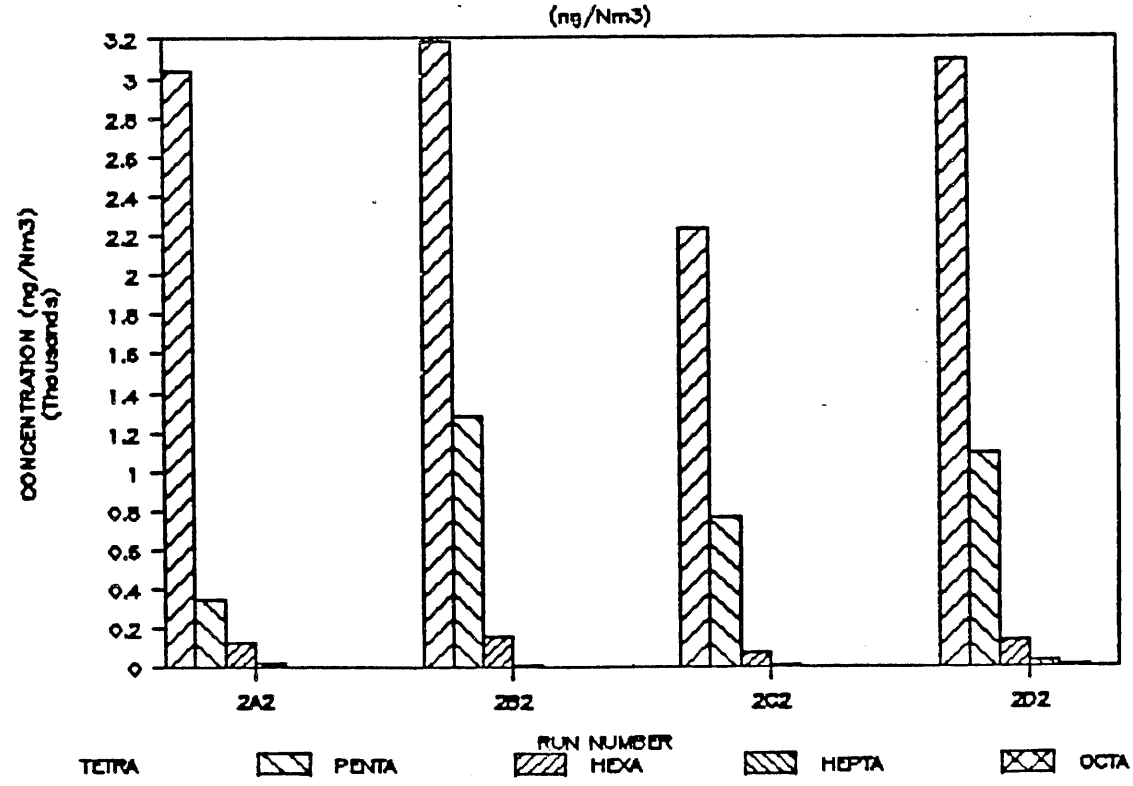


FIGURE 6.5-5 PCDF HOMOLOGUE DISTRIBUTION



PCDF HOMOLOGUE DISTRIBUTION



theory that longer retention times because of low boiler temperatures contributed to this dechlorination effect. Commoner et al. (1985) cite the work of Niessen in suggesting that there is a strong positive correlation between PCDD/PCDF concentrations and the square of the available HCl. They go on to indicate that the creation of higher chlorinated compounds is limited by HCl levels. A quick review of HCl levels in Toronto and Hamilton (Ozvacic et al., 1985) illustrates this hypothesis:

- Toronto HCl emissions 12.4-12.8 g/s and hexa compounds dominate;
- Hamilton HCl emissions 5.9-8.3 g/s and tetra compounds dominate.

Examination of HCl levels at location A shows available HCl levels of 1.97 g/s, thus the Japanese data follow the reported trend. The PEI data showed OCDDs and HxCDFs to be the dominant homologues. The average HCl emission rate at PEI was 4.5 g/s (CSC, 1985). Data from Quebec City APC tests shows HpCDD and TCDF to dominate for all runs except the high temperature (>400°F) dry reactor runs, where PeCDF was dominant. These runs had the lowest average incoming HCl concentration 0.4 g/s, accompanied by the lowest incoming average temperature and moisture.

The homologue distribution data shows that the Japanese data are not out of line with some other results but suggests that several factors may play a role in the results. Among these factors are:

- residence time,
- temperature,
- available HCl levels, and
- availability of phenolic precursors

The HCl levels reported in the data relate to residual HCl values not the amount of HCl available for reaction. Thus lower levels of HCl emissions would not necessarily result in lower levels of PCDD/PCDF chlorination. HCl measurements also do not address the levels of available Cl_2 versus HCl. Doyle et al. (1986) note combustion conditions directly influence

the HCl versus Cl_2 split, with higher excess air levels leading to higher production levels of Cl_2 than HCl.

A balance exists between all these factors and until more laboratory work can provide a better understanding of the relationships, and this theory can be transferred to full scale incinerators, more detailed hypotheses will not provide the answers. The homologue distributions illustrate, however, that the PCDD/PCDF materials found both before and after the fabric filter have a higher volatility than those found at P.E.I., for instance. This volatility, combined with the temperatures that the Japanese APC system operated at, may shed some light on why the results were as noted.

Comparing the performance of the Japanese system with the test data from Quebec City shows some interesting parallels. The Japanese system operated with temperatures of 680°F entering, 500°F after quench reactor, 440°F after the venturi and 390°F at the exit (2D2 averages). The Quebec system at high temperature ran 500°F inlet, 400°F after the dry reactor and 360°F at the exit. In wet slurry injection mode, by-passing the dry reactor, the system temperatures were 505°F, 282°F and 275°F at the inlet, the fabric filter inlet and the exit respectively. These two configurations can be compared to the Japanese data.

In the Quebec City slurry injection system the total PCDD/PCDF concentration went from 1760 ng/Nm^3 @ 8% O_2 to 1830 ng/Nm^3 @ 8% O_2 across the reactor. In the Japanese test the change was 4433 to 5194 ng/Nm^3 @ 12% CO_2. Thus, neither wet slurry system removed PCDDs/PCDFs. In the Quebec dry system, with the quench tower used as a point for water cooling addition, no PCDDs/PCDFs were removed during the runs at temperatures comparable to the Japanese data.

Removal efficiencies at Quebec City were gained solely on the fabric filter. Surprisingly, across the dry venturi, the Japanese plant shows a 21% reduction in concentration. With no means of removing material from

the system this result would appear anomalous, however, the consistent reduction in both PCDDs and PCDFs shown at this point is most likely attributable to the imprecision in measurement and analysis. Particulate matter concentrations did not exhibit the same behaviour further confirming the validity of the analysis variation argument. No detectable PCDDs/PCDFs exited the Quebec system during the wet slurry injection mode and only 7 ng/Nm^3 @ 8% O_2 were found in the exhaust during the high temperature dry mode. This performance (99.9956% removal) suggests that the poor particulate capture efficiency of the Japanese baghouse is, at least in part, a contributor to the high exhaust concentrations of PCDDs/PCDFs. The removal efficiency for the fabric filter (2C2 to 2D2) was reported earlier at 94.85% and thus, one would have anticipated approximately 180 ng/Nm^3 @ 12% CO_2 total PCDD/PCDF to be emitted from the stack based upon a mass balance with the inlet concentration. The actual test value is 7003 ng/Nm^3 @ 12% CO_2 (2D2).

Temperature becomes an important parameter in understanding the behaviour of the systems. Stieglitz (1985) as cited by Karasek and Hutzinger (1986) reported results of laboratory studies on the thermal behaviour of PCDDs on flyash from an MSW incinerator. When heated to 250-350°C (482-662°F) PCDD concentrations went from 350 ppb to 3900 ppb. Above 400°C (752°F) 50% of the PCDD is released into the gas phase. As temperature continues to climb, dechlorination takes place with the OCDD and HpCDD shifting to lower levels. At 500°C (932°F) the flyash suffers extensive decomposition of PCDDs and the residual concentration is 15 ppb. This suggests that the temperature of the gas leaving the Japanese incinerator is at the top of the range for rapid synthesis of PCDD compounds. Even after passing through the quench reactor the temperature is still in the "generation" range, thus the increase in PCDD/PCDF concentration even with the removal of 48 µg/Hr. of PCDDs/PCDFs from the quench reactor hopper.

Commoner et al. (1985) uses Eiceman's data to argue that the material bound to the surface of particles at temperatures above 250°C is

irreversibly bound until the temperature rises appreciably. Clearly this is the material that the fabric filter could trap and retain. This chemisorbtion theory is also discussed by Shaub (1984). Commoner et al. goes on to say that between 100°C (212°F) and 200°C (392°F) both chemisorption and adsorption occur. They state that the latter situation is easily reversible, the former requires higher temperatures to reverse. This suggests that, at the operating temperatures in the Japanese APC, it would be possible to adsorb PCDDs/PCDFs to flyash, lime and Tesisorb. These may chlorinate to higher levels in the presence of HCl or Cl_2 and would be captured on the filter bags. Some of this material would not desorb due to the nature of the bond, but other materials will elute over time and pass through the filter. Given the previously advanced hypothesis that the majority of the materials released from the fabric filter are extremely fine, the desorbtion mechanism does not even have to take place. The fines with their attached PCDDs/PCDFs, would work their way through the bag material over time.

A definite time constant will exist for this process. Since the bags are cleaned on a two to three hour rotation, some material may have been present on the bag for up to three hours. Given the incidence of noticeably poor combustion in the hours preceding run 2D2 it is likely that over half the bag catch contains materials trapped during the excursion. Chemical kinetics can be used to explain both the synthesis of PCDDs/PCDFs at temperatures below 1000°F and their destruction above 1500°F. The combination of generation and destruction is a yet to be defined parameter for most incinerators and is a function of mixing and residence time. The data can however suggest, however, that during the low temperature excursion at 0400 on 10/14/83, large amounts of PCDDs/PCDFs could have been created. This quantity likely exceeded those quantities being produced during the test period and captured at sampling point A, B and C.

Examination the Japanese data for the two hours preceding the second test, would suggest that stack moisture levels should have dropped.

Test data reveal that this is the case and the second test is approximately 7% lower at A and B and 4.5% at D. Since some delay time is bound to have occurred in stack gas moisture gain, it is likely that at the start of the second test period the moisture levels were even lower and the readings being recorded for the second test series are an average of start and finish values. Lower moisture levels may reduce agglomeration as well as influencing PCDD/PCDF removal effectiveness. These factors combined, could have lead to the higher emissions recorded on 2D2 but, as has been explained, this behaviour is also an artifact of system performance in the period preceding the testing. The hypothesis could be reviewed if real time data for water flow and temperatures were available from MHI.

In conclusion, the results of the PCDD/PCDF emissions tests have been reviewed and shown to be representative of the situation occurring at the time of the tests. The high exit PCDD/PCDF levels are higher than would have been anticipated based upon comparison to Quebec City APC results (NITEP, 1986), but these data are explainable by the previous history of material on the bags. Other studies since the date of the Japanese tests have found that PCDD/PCDF levels can increase as the gases are cooled and show the need for both good combustion and new pollution control equipment as viable means of controlling PCDD/PCDF emissions from MSW incinerator facilities.

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FINAL REPORT

THE RESULTS OF ANALYSES OF COMBUSTION PRODUCTS COLLECTED DURING TESTS OF A REFUSE-FIRED INCINERATOR LOCATED IN TSUSHIMA, JAPAN FOR POLYCHLORINATED DIBENZODIOXINS AND DIBENZOFURANS, SELECTED METALS AND FLUORIDES/CHLORIDES

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July 14, 1984

I. INTRODUCTION

In the summer of 1983, Cooper Engineers of Richmond, California and the Brehm Laboratory of Wright State University, Dayton, Ohio, jointly proposed a sampling and analysis program to study the combustion products from a refuse-fired incinerator, in order to determine the content of polychlorinated dibenzodioxins and dibenzofurans, selected metals and fluorides/chlorides. This proposal was submitted to the State of California Air Resources Board (CARB) and the Ministry of the Environment (MOE), Province of Ontario, Canada, and the incinerator to be tested was located in Tsushima, Japan. This incinerator was of interest because it was equipped with several different types of emission control equipment, which were possible candidates for use in the U.S. and Canada. The proposal was subsequently funded by CARB and MOE through a prime contract with Cooper Engineers. The Brehm Laboratory accomplished work on this project under a sub-contractual agreement with Cooper Engineers dated December 20, 1983.

Cooper Engineers, in conjunction with Chemecology Corporation, was responsible for the sampling of the Japanese incinerator. The Brehm Laboratory accomplished all analyses of the combustion products collected by Cooper. Sampling tests were conducted in Tsushima, Japan in October, 1983 and samples were provided to the Brehm Laboratory in early November, 1983.

The present report describes in detail the elaborate analytical procedures implemented by the Brehm Laboratory for the combustion product analyses and summarizes the results obtained.

II. SAMPLES PROVIDED TO THE BREHM LABORATORY FOR ANALYSES

A detailed description of the incinerator tested and of the sampling procedures utilized by Cooper Engineers in the emissions testing conducted at the Tsushima, Japan facility are provided in Cooper Engineers' portion of the report on this project. For the present report, it is sufficient to note that both modified EPA Method 5 and Method 17 sampling trains were used to sample the incinerator emissions at four different locations (designated A, B, C, and D, respectively) and these trains ultimately yielded several different types of samples for analyses. The types of samples resulting from the Cooper Engineers' tests which were provided to the Brehm Laboratory are listed below. The number of each type of sample received is indicated in parentheses following the sample type.

1. Particulate filters (9)
2. Acetone rinse of probe and nozzle (also contains particulates) (9)
3. Toluene rinse of probe and nozzle (9)
4. Impinger liquids (14)
5. Acetone rinse of impingers (9)
6. Toluene rinse of impingers (9)
7. XAD-2 resin traps (18)
8. Multi-Clone particulate fractions and filters (15)

9. Ash samples (3)
10. Acetone prewash of sampling train (1)
11. Toluene prewash of sampling train (1)

Total Samples Provided for Analyses 97

Some of these samples were analyzed for polychlorinated dibenzo-p-dioxins (CDDs) and dibenzofurans (CDFs), others were analyzed for selected metals, and portions of some samples were analyzed for fluorides and chlorides. In addition, the weights of total particulates collected in each sampling test, and the weights of the residues resulting from concentration of a portion of the impinger liquids to dryness were determined. The sample preparation and analytical procedures utilized are described below.

III. SAMPLE PREPARATION AND ANALYSIS PROCEDURES AND RESULTS OF ANALYSES

A. Measurement of Volumes of Liquids Received.

The glass vessels containing the liquid samples obtained using the sample recovery procedures applied by Cooper Engineers/Chemecology to the trains used to collect emission products from the incinerator were marked by Cooper to indicate the original level of liquids in the bottles at the time of filling. Upon receipt of the samples at the Brehm Laboratory, it was visually evident by comparing the liquid levels in the sample vessels with the fill lines which had been marked on these bottles that loss of liquids had occurred in some samples. Since it could not be determined whether these losses were due to evaporation of solvents or to leakage from the bottles, no correction of the analytical data for these losses was possible. However, the volume of each liquid sample received was determined using a graduated cylinder and, after removing the actual sample, the volume of liquid required to fill the sample bottle to the original fill line was also determined. These data are summarized in Table 1. As can be seen, there was no consistent pattern for the samples for which liquid losses were apparent. For example, not all such losses occurred from the sample bottles containing the most volatile solvent (acetone). Consequently, it is probable that physical leakage of liquids from the bottles accounted for most of the observed losses.

B. Determination of Particulate Weights.

Particulates collected from the flue gases are present in three types of the train samples, that is, the particulate filters of the M-5 and M-17 trains, the Multi-Clone sized-particulate fractions from those tests in which the Multi-Clone sampler was used, and the acetone rinses of the sampling probe and nozzle section of the train. The particulates collected on the filters were provided along with the filters themselves either in sample bottles or in Petri dishes. Upon receipt at the Brehm Laboratory, the sample vessels were opened and each open vessel, with the filter and particulate inside, was placed in a closed dessicator containing a moisture sorbing material (Drierite). After standing for several hours, typically 12-16 hours, each sample vessel containing the filter and particulate was removed and weighed. The drying and weighing procedures were then repeated until the

weight of each sample vessel (and contents) was constant within 5%, in two successive weighings. The filter and particulates from each bottle were then removed to another sample bottle and the original vessel was rinsed with a small volume of toluene and dried. The original vessel was then weighed. The tare weight of each original particulate filter, obtained by Chemecology prior to use in the sampling train, and provided to the Brehm Laboratory, was then added to the weight of the sample vessel and this weight was subtracted from the combined weight of the original sample vessel, the filter and the particulates to obtain the weight of particulates only in each case.

The weights of particulates in the acetone probe and nozzle rinses of the Method 5 and Method 17 Sampling Trains were determined by concentrating each rinse solution to dryness in a previously tared sample vessel, (using a stream of dry nitrogen while heating the sample vessel to 55°C in a water bath) and weighing the bottle and residual particulate, then subtracting the vessel weight to obtain the weight of particulate only. The weight of this particulate was then added to the weight of particulate collected on the filter for the corresponding sampling train to arrive at the total particulate weights for each of the M-5 and M-17 sampling train tests and these particulate weights are listed in Table 2.

The weights of the particulates in each of the sized fractions collected with the Multi-Clone sampler are shown in Table 3.

C. Determination of Condensible Residues in Impinger Liquids.

An aliquot of each of the combined impinger solutions from each sampling train was transferred to a separate tared sample vessel and the liquid was evaporated by passing a gentle stream of dry nitrogen over the liquid while heating the sample bottle in a heat bath. When the solution had been concentrated to dryness, the sample vessel and residue were again weighed and the weight of the bottle was subtracted to obtain the weight of condensable residue. These weights are listed in Table 4 for each of the impinger solutions.

D. Determination of Chloride and Fluoride Concentrations in Impinger Liquids.

An aliquot (one-half) of the combined impinger liquids from each sampling train was extracted as described in Section F below to remove organic constituents. The residual aqueous fraction was then analyzed for chloride and fluoride content. These analyses were accomplished by Howard Laboratories, Dayton, Ohio, a laboratory certified by the Ohio EPA, working under subcontract to the Brehm Laboratory of Wright State University. The procedures utilized for the fluoride analyses were as described in the U.S. EPA Methods for Chemical Analysis of Water and Waste, March, 1979, Section 240.1 and 340.2. Fluoride concentration was measured with an Orion Model-901 Millivolt/pH Meter, fitted with a Model 9409 Fluoride electrode and a Model 9401 Reference electrode. Procedures used for chloride analyses were as described in the U.S. EPA Methods for Chemical Analyses of Water and Wastes, March, 1979, Section 325.3. This procedure is effectively a titrimetric method.

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the metals measured
are reported.

weight of each sample vessel (and contents) was constant within 5%, in two successive weighings. The filter and particulates from each bottle were then removed to another sample bottle and the original vessel was rinsed with a small volume of toluene and dried. The original vessel was then weighed. The tare weight of each original particulate filter, obtained by Chemecology prior to use in the sampling train, and provided to the Brehm Laboratory, was then added to the weight of the sample vessel and this weight was subtracted from the combined weight of the original sample vessel, the filter and the particulates to obtain the weight of particulates only in each case.

The weights of particulates in the acetone probe and nozzle rinses of the Method 5 and Method 17 Sampling Trains were determined by concentrating each rinse solution to dryness in a previously tared sample vessel, (using a stream of dry nitrogen while heating the sample vessel to 55°C in a water bath) and weighing the bottle and residual particulate, then subtracting the vessel weight to obtain the weight of particulate only. The weight of this particulate was then added to the weight of particulate collected on the filter for the corresponding sampling train to arrive at the total particulate weights for each of the M-5 and M-17 sampling train tests and these particulate weights are listed in Table 2.

The weights of the particulates in each of the sized fractions collected with the Multi-Clone sampler are shown in Table 3.

C. Determination of Condensible Residues in Impinger Liquids.

An aliquot of each of the combined impinger solutions from each sampling train was transferred to a separate tared sample vessel and the liquid was evaporated by passing a gentle stream of dry nitrogen over the liquid while heating the sample bottle in a heat bath. When the solution had been concentrated to dryness, the sample vessel and residue were again weighed and the weight of the bottle was subtracted to obtain the weight of condensable residue. These weights are listed in Table 4 for each of the impinger solutions.

D. Determination of Chloride and Fluoride Concentrations in Impinger Liquids.

An aliquot (one-half) of the combined impinger liquids from each sampling train was extracted as described in Section F below to remove organic constituents. The residual aqueous fraction was then analyzed for chloride and fluoride content. These analyses were accomplished by Howard Laboratories, Dayton, Ohio, a laboratory certified by the Ohio EPA, working under subcontract to the Brehm Laboratory of Wright State University. The procedures utilized for the fluoride analyses were as described in the U.S. EPA Methods for Chemical Analysis of Water and Waste, March, 1979, Section 240.1 and 340.2. Fluoride concentration was measured with an Orion Model-901 Millivolt/pH Meter, fitted with a Model 9409 Fluoride electrode and a Model 9401 Reference electrode. Procedures used for chloride analyses were as described in the U.S. EPA Methods for Chemical Analyses of Water and Wastes, March, 1979, Section 325.3. This procedure is effectively a titrimetric method.

The samples provided to Howard Laboratories by the Brehm Laboratory were identified only by code numbers. In addition to the impinger liquid samples, the Brehm Laboratory prepared and submitted for chloride and fluoride analyses a blank (distilled water) sample and a spiked water sample containing 261 μg/mL of chloride and 1.90 μg/mL of fluoride. These samples were submitted in blind fashion, identified only by code numbers and were indistinguishable from the impinger liquids to Howard Laboratories analysts. The latter samples were, of course, intended to provide a Quality Assurance performance check on Howard Laboratories analyses.

The results of the chloride/fluoride analyses are listed in Table 5. As can be seen, the data obtained for the blank and spiked samples were quite acceptable. In addition, the results obtained for two duplicate analyses of impinger liquid samples (again submitted separately and identified by different code numbers to Howard Laboratories) indicate that the replicability of Howard Laboratories is excellent (the differences in replicate analyses ranging from 1.2% at the 500 μg/mL concentration to 20% at the 0.5 μg/mL concentration).

E. Determination of the Concentration of Selected Metals in the Sized Particulate Fractions Collected with the Multi-Clone Sampler.

The sized particulate fractions were initially extracted as described in Section F below to remove organic constituents. The residual fractions were then submitted to Howard Laboratories for determination of the content of selected metals. The analytical procedures utilized were those specified in the U. S. EPA Methods for Chemical Analysis of Water and Wastes, March 1979, Section 200.0. These procedures utilize Atomic Absorption Spectrometry to measure the metal concentrations, and an Instrumentation Laboratory Model No. IL-357 was employed for the analyses reported here.

The particulate fraction samples submitted to Howard Laboratories were identified only by coded numbers. Included among these samples was a Performance check sample (but not identified as such to the analyzing laboratory) which consisted of an aliquot of National Bureau of Standards Fly Ash, for which certified analytical data on metal concentrations are provided by NBS.

The results of the particulate fraction analyses for metals are presented in Table 6. In all cases except one, the 3D1 samples, each of the three sized particulate fractions was analyzed separately. The three sized fractions from the 3D1 test, however, were too small in quantity to analyze separately, and these fractions were therefore combined into a single sample for analyses. In addition, the filter sample from the 3D1 test was apparently partially burned during the sampling test and only a portion of the residual filter was received by the Brehm Laboratory. Therefore, it was not possible to obtain a reliable weight for the particulate fraction collected on the filter in the 3D1 test, and so only the total quantities of the metals measured in the combined sample (and not the concentrations) are reported.

The results reported by Howard Laboratories for the NBS Fly Ash sample are in reasonable agreement with the NBS Certified concentrations of metals in this sample for all metals except As and Cr. Data reported by Howard Laboratories for the latter are substantially lower than expected. Presumably, this reflects limitations of the analytical procedures with respect to the metals.

F. Determination of Chlorinated Dibenzo-p-dioxins and Dibenzofurans in Samples from M-5 and M-17 Sampling Trains and from Multi-Clone Samplers.

1. Combining of Train Samples for CDDs/CDFs Analyses

Some of the individual samples from each sampling train were combined to create either three or four samples from each train for analysis to determine the content of polychlorinated dibenzo-p-dioxins (CDDs) and dibenzofurans (CDFs). In the case of the M-5 train sampler, the particulate filter and the toluene probe end nozzle rinse from each train were combined to create one sample. This was accomplished by using the toluene rinse liquid as the extracting liquid in a Soxhlet apparatus, in which the particulate was extracted. The Soxhlet extraction procedure is described in greater detail below. The particulate residue from the acetone probe and nozzle rinse (obtained as described in Section III.B above) from the M-5 train was analyzed separately in the present program, and again was Soxhlet extracted. The third sample from the M-5 train which was prepared for analysis was obtained by combining the impinger liquids with the acetone and toluene impinger rinses. This was achieved by first combining the toluene and acetone rinses and concentrating these to near dryness using a stream of dry nitrogen while heating the sample vessel in a 55°C water bath. The residue was reconstituted by adding 40 mL of hexane. One-half of this solution was then added to one-half of the combined impinger liquids, and the mixture was agitated in order to extract the organic components from the aqueous impinger liquid into the hexane phase. The hexane phase was then removed and analyzed for CDDs/CDFs, while the aqueous phase was analyzed for chlorides and fluorides, as described in Section D above. The fourth sample from each M-5 train which was analyzed for CDDs/CDFs was the XAD-2 resin trap. For all of the M-5 tests, only the front (or first) XAD-2 trap was analyzed. Again, analyses entailed Soxhlet extraction of a portion of the resins, as described in greater detail below.

Combining of samples from the M-17 trains for CDDs/CDFs analyses was accomplished somewhat differently than for the M-5 train samples. In the former case, the M-17 particulate filter (and particulates thereon) was Soxhlet extracted and analyzed as a separate sample for CDDs/CDFs. The acetone and toluene probe and nozzle rinses and the acetone and toluene impinger rinses were combined with the impinger liquids (in a manner similar to that described above for the corresponding M-5 train samples) to yield a second sample for CDDs/CDFs analyses. Finally, the XAD-2 trap was analyzed. In one M-17 test (2A1) only the front XAD-2 trap was analyzed, whereas in the second M-17 test, both front and back XAD-2 traps were analyzed.

While the impinger liquids from the separate impingers on most of the trains were combined prior to CDDs/CDFs analyses, as already noted, in one case (test 2D2), the impinger contents in separate impingers were separately analyzed. Three different fly ash samples from these tests were also analyzed separately, as were acetone and toluene samples from prewashing of a sample train prior to use in the testing.

2. Sample Extraction Procedures

a. Liquid Samples (Combined Impinger Liquids and Rinses). One-half of the impinger liquids and hexane, prepared as described in Section F1 above, are placed in a clean 500 mL amber glass bottle. Appropriate quantities of the isotopically-labelled internal standards, $^{13}C_{12}$-2,3,7,8-Tetra-CDD, $^{37}Cl_4$-1,2,3,4,6,7,8-Hepta-CDD, and $^{13}C_{12}$-Octa-CDD, are added to the bottle (for quantities added to each sample in the present analyses, see the Sample Tracking Forms in Appendix B of this report) and the bottle is sealed with a Teflon-lined cap. The bottle is then attached to a laboratory shaker and agitated vigorously for a period of three hours. The aqueous and organic phases are then allowed to separate and the organic phase is removed and transferred to a clean 250 mL glass bottle. Proceed with the extract cleanup phase (Section F3 below).

b. Solid Samples (Particulate Filters, Particulate Fractions, XAD-2 Resin. Solid samples are extracted in a Soxhlet apparatus. For the particulate filters and particulate fractions, the entire sample of each is placed in the glass thimble of the Soxhlet. In the case of the XAD-2 resins, these are removed from the traps and one-half of the sample (accurately weighed) is placed in the glass Soxhlet thimble. In the case of all samples, the isotopically-labelled internal standards, as specified in Section F2a above, are added to each sample in the glass Soxhlet thimble. The Soxhlet thimble is inserted into the Soxhlet apparatus, the reservoir is charged with toluene, and heat is applied to the reservoir to cause refluxing of the toluene, extracting the sample. Refluxing is continued for a period of 16 hours. Particulates and particulate filters are extracted with 75 mL of toluene (if necessary additional toluene is added to the toluene rinse solutions with which these are extracted, as described in Section F1 above). XAD-2 resin samples are extracted with 150 mL of toluene.

For ash samples, an accurately weighed aliquot of the sample is placed in the Soxhlet thimble, spiked with internal standards and extracted with 75 mL of toluene as described above.

The toluene extract resulting from the Soxhlet extraction is concentrated to a volume of about 5 mL using a Snyder column, and the residue is transferred (with three rinsings) to a clean 125 mL glass bottle. Hexane (40 mL) is then added to the bottle. Proceed with the extract cleanup phase (Section F3 below).

3. Clean-up and Liquid Chromatographic Separation.

a. Add 50 mL of doubly distilled water to the vessel containing the sample extract, reseal the vessel and agitate for 10 minutes. Allow the vessel to stand for a period sufficient for the aqueous and organic layers to separate completely, and remove and discard the aqueous layer.

b. Using the same procedure as applied in 3a., wash the extract successively with 50 mL portions of 50% KOH, doubly distilled water, concentrated H_2SO_4 (except in this case agitate mixture for 15 min.), and doubly distilled water, in each case discarding the washing agent. The acid washing procedure with concentrated sulfuric acid is repeated until the acid layer is visually colorless.

c. Add 5 g of anhydrous sodium sulfate to the washed extract and allow to stand in order to remove residual water. Transfer the extract to a centrifuge tube and concentrate to near dryness by placing the tube in a water bath at 55°C, and passing a gentle stream of filtered, pre-purified N_2 over the solution.

d. Prepare a glass macro-column, 20 mm OD x 230 mm in length, tapered to 6 mm OD on one end. Pack the column with a plug of silanized glass wool, followed successively by 1.0 g silica, 2.0 g silica containing 33% (w/w) 1M NaOH, 1.0 g silica, 4.0 g silica containing 44% (w/w) concentrated H_2SO_4 and 2.0 g silica. Quantitatively transfer the concentrated extract from Step c. to the column and elute with 90 mL hexane. Collect the entire eluent and concentrate to a volume of 1-2 mL in a centrifuge tube, as before.

e. Construct a disposable liquid chromatography mini-column by cutting off a Pyrex 10 mL disposable pipette at the 2.0 mL mark and packing the lower portion of the tube with a small plug of silanized glass wool, followed by one gram of Woelm basic alumina, which has been previously activated for at least 16 hours at 600°C in a muffle furnace, and cooled in a dessicator for 30 minutes just prior to use. Quantitatively transfer the concentrate from Step d. onto the liquid chromatography column, rinse the centrifuge tube consecutively with two 0.3 mL portions of 3% CH_2Cl_2-in-hexane, and also transfer the rinses to the chromatography column.

f. Elute the column with 5 mL of 3% (v/v) CH_2Cl_2-in-hexane and retain the eluent for PCB analysis.

g. Elute the column with 20 mL 50% (v/v) CH_2Cl_2-in-hexane and retain the eluent to check for retention of CDDs and CDFs on the column.

h. Concentrate each of the retained fractions to a volume of approximately 1 mL by heating the tubes in a water bath while passing a stream of prepurified N_2 over the solutions, as described above. Quantitatively transfer the concentrated fractions into separate 2 mL micro-reaction vessels, splitting each fraction so that one-half goes into each of two sample vessels. (The contents of one vessel are analyzed for CDFs, and the contents of the other for CDDs). Evaporate the solutions in each of the micro-reaction vessels almost to dryness, using the procedures just mentioned, rinse the walls of each vessel down with 0.5 mL CH_2Cl_2, and reconcentrate just to dryness.

i. Approximately 1 hour before gas chromatographic-mass spectrometric (GC-MS) analysis, dilute the residue in each micro-reaction vessel with an appropriate quantity of benzene (depending upon the anticipated quantities of analytes in each vessel) and gently swirl the solvent in the vessel to ensure dissolution of CDDs, CDFs and PCBs. Inject an appropriate aliquot of this solution into the GC-MS instrument.

4. Procedures for Gas Chromatographic-Mass Spectrometric (GC-MS) Analysis

a. Parameters for High Resolution Gas Chromatographic Low Resolution Mass Spectrometric (GC-LRMS) Analysis

This procedure can be used both for screening samples for "total" CDDs and CDFs by chlorinated class (mono-, di-, etc., through octachlorinated) as well as for determining certain specific CDD and CDF isomers (for example, the 2,3,7,8-TCDD isomer) in cases where complete resolution of such isomers can be demonstrated.

1) Instrumentation: Perkin Elmer Sigma III Gas Chromatograph coupled through a custom-fabricated interface including a single-stage glass jet separator to a Kratos MS-25 Mass Spectrometer equipped with a DS-55SM Data System.

2) Parameters for the Gas Chromatograph:

Column:	60 M WCOT DB-5 Silica Capillary
Carrier Gas:	Hydrogen, 30 lb. head pressure
Column Temperature:	Programmed, see Table A for temperature program.
Interface Temperature:	250°C
Injector:	Splitless Injection

3) Parameters for the Mass Spectrometer:

Selected Ion Monitoring Mode (for m/z's monitored and details of instrumental procedures see Table A)

Ionizing Voltage:	70 eV
Accelerating Voltage:	4 KV

4) Date Acquisition/Handling:

The DS55SM Data System and associated peripherals were employed to acquire both analog (total ion current plots, specific ion current monitoring plots) and digital (peak areas) data, from which the quantities of PCDD/PCDF present in the samples were calculated.

TABLE A. Sequence of Operations in GC-MS-DS Quantitation of CDDs/CDFs in Extracts of Environmental Samples

Elapsed Time (min)	Event	GC Column Temperature (°C)	Temperature Program Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approximate Theoretical Ratio of $[M]^+$:$[M+2]^+$
0.00	Injection, splitless	190					
1.00	Turn on split valve	190					
1.00	Begin temp. program to 220°C	190	5				
6.00	Open column flow to mass spectrometer	215	5				
7.00	Column temperature hold	220					
14.00	Start Tetra Program; sweep = 350 ppm; time/mass = 0.08 sec.			240.938	$[M-COCl]^+$	TCDF	
				258.930	$[M-COCl]^+$	TCDD	
				303.902	$[M]^+$	TCDF	
				305.899	$[M+2]^+$	TCDF	
				319.897	$[M]^+$	TCDD	0.77
				321.894	$[M+2]^+$	TCDD	1.00
				327.885	$[M]^+$	$^{37}Cl_4$-TCDD	
				331.937	$[M]^+$	$^{13}C_{12}$-TCDD	
				373.840	$[M]^+$	HxDPE[a].	
22.00	Stop Tetra Program	220					
22.50	Start Penta Program; sweep = 350 ppm; time/mass = 0.12 sec.			274.899	$[M-COCl]^+$	PeCDF	
				290.894	$[M-COCl]^+$	PeCDD	
				337.863	$[M]^+$	PeCDF	
23.00	Begin temp. program to 235°	220	5	339.860	$[M+2]^+$	PeCDF	
26.00	Column temperature hold	235		353.858	$[M]^+$	PeCDD	0.57
				355.855	$[M+2]^+$	PeCDD	1.00
				407.801	$[M]^+$	HpDPE[a].	
32.00	Stop Penta Program						
32.50	Start Hexa Program; sweep = 350 ppm; time/mass = 0.20 sec.	235		310.857	$[M-COCl]^+$	HxCDF	
				326.852	$[M-COCl]^+$	HxCDD	
				373.821	$[M]^+$	HxCDF	
				375.821	$[M+2]^+$	HxCDF	
				389.816	$[M]^+$	HxCDD	1.00
				391.813	$[M+2]^+$	HxCDD	0.87
				443.759	$[M]^+$	ODPE[a].	

TABLE A. Sequence of Operations in GC-MS-DS Quantitation of CDDs/CDFs in Extracts of Environmental Samples (Cont.)

Elapsed Time (min)	Event	GC Column Temperature (°C)	Temperature Program Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approximate Theoretical Ratio of $[M]^+$:$[M+2]^+$
33.00	Begin temp. program to 250°C	235	5				
36.00	Column temperature hold	250					
42.50	Stop Hexa Program						
43.00	Start Hepta Program; sweep = 350 ppm; time/mass = 0.30 sec.	250		344.818	$[M-COCl]^+$	HpCDF	
				360.813	$[M-COCl]^+$	HpCDD	
				407.782	$[M]^+$	HpCDF	
				409.779	$[M+2]^+$	HpCDF	1.00
				423.777	$[M]^+$	HpCDD	1.00
				425.774	$[M+2]^+$	HpCDD	
				477.720	$[M^+]$	NDPE[a].	
53.00	Stop Hepta Program	250		431.765	[m+]	$^{37}Cl_4$-HpCDD	
53.50	Start Octa Program; sweep = 350 ppm; time/mass = 0.30 sec.	250		378.768	$[M-COCl]^+$	OCDF	
				394.774	$[M-COCl]^+$	OCDD	
				441.732	$[M]^+$	OCDF	
54.00	Begin temp. program to 270°	250°	5	443.740	$[M+2]^+$	OCDF	
58.00	Column temperature hold	270°					
				457.738	$[M]^+$	OCDD	0.86
				459.735	$[M+2]^+$	OCDD	1.00
				469.779	$[M]^+$	$^{13}C_{12}$-OCDD	
				471.776	$[M+2]^+$	$^{13}C_{12}$-OCDD	
				511.681	$[M]^+$	DDPE[a].	
65.00	Stop Octa Program						
65.00	Begin temp. program to 300°	270°	5				
71.00	Column temperature hold	300°					
75.00	Cool Column to 190°						

[a] HxDPE, HpDPE, ODPE, NDPE, DDPE are abbreviations which designate (respectively) hexachloro-, heptachloro-, octachloro-, nonachloro-, and decachlorodiphenyl ethers.

5. Reagents and Chemicals

The following is a listing of the reagents and chemicals utilized in the procedures outlined above. Potassium hydroxide, anhydrous sodium sulfate, hydrochloric acid, and sulfuric acid were all Reagent Grade and were obtained from J. T. Baker Chemical Co. or Fisher Scientific Co., Fairlawn, N.J. Methanol, hexane, methylene chloride and benzene were "Distilled in Glass" quality obtained from Burdick and Jackson, Muskegon, Michigan. Woelm basic alumina (Activity Grade I) was obtained from ICN Pharmaceuticals, Cleveland, Ohio. Silica (Bio-Sil A) was obtained from Bio-Rad, Rockville Centre, New York. Doubly distilled water was obtained using the all-glass distillation apparatus in the Brehm Laboratory. Prepurified nitrogen was obtained from Airco, Inc., Montvale, New Jersey. Ethanol, "Pesticide Quality", was obtained from Curtin-Matheson Scientific, Cincinnati, Ohio.

CDDs/CDFs Standards employed in this work were obtained from the sources listed below:

$^{37}Cl_4$-2,3,7,8-TCDD: KOR Isotopes, Cambridge, Mass.

$^{13}C_{12}$-2,3,7,8-TCDD: Cambridge Isotope Laboratories, Cambridge, Mass.

All 22 TCDD Isomers: Brehm Laboratory, Wright State University, Dayton, Ohio

1,2,3,7,8-PCDD: Brehm Laboratory, Wright State University, Dayton, Ohio

1,2,3,4,7,8-HxCDD: Brehm Laboratory, Wright State University, Dayton, Ohio

1,2,3,4,6,7-HxCDD: KOR Isotopes, Cambridge, Mass.

$^{37}Cl_4$-1,2,3,4,6,7,8-HpCDD: KOR Isotopes, Cambridge, Mass.

1,2,3,4,6,7,8-HpCDD: KOR Isotopes, Cambridge, Mass.

OCDD: Analabs, Inc., North Haven, Connecticut

$^{13}C_{12}$-OCDD: KOR Isotopes, Cambridge, Mass.

2,3,7,8-TCDF: Cambridge Isotope Laboratories

$^{37}Cl_4$-2,3,7,8-TCDF: KOR Isotopes, Cambridge, Mass.

1,2,4,7,8-PCDF: U.S. FDA, Wash., D.C.

1,2,4,6,7,9-HxCDF: U.S. FDA, Wash., D.C.

1,2,3,4,6,8,9-HpCDF: U.S. FDA, Wash., D.C.

OCDF: U.S. FDA, Wash., D.C.

6. GC/MS Calibration Procedures for CDDs/CDFs and Quantitative Analyses of Sample Extracts.

a. Tetra-through octa-CDD and -CDF include 136 separate isomers (49 CDD and 87 DCF). Since truly quantitative isomer specific analyses for all of these isomers are not presently practical, and were not intended as the objective of the analyses accomplished here, the method utilized here was based on calibration of the GC/MS instrumentation for only selected CDD/CDF isomers which are presumed to be representative of all of the other isomers. Calibration of the GC/MS system, therefore, initially entails characterization of the CDD/CDF standards selected which represent each class of isomers (the degree of chlorination, monochloro- dichloro-, etc., defines the "class" of isomers) known to comprise the group of compounds being determined. The following procedure for characterization of the representative CDD/CDF isomers was applied.

1) Obtain mass spectra for each isomer standard utilized (see list of standards in Section F5 above) noting in particular the relative abundances of the m^+ and $m+2^+$ peaks.

2) Determine gas chromatographic retention times for each isomer standard used.

3) Based on the above data, select the ion masses appropriate for detecting and quantifying the isomers in the class of interest, and select the gas chromatographic retention time window appropriate for all isomers in that class (that is, the time interval during which the earliest-eluting and latest-eluting isomers of a particular class elute from the gas chromatographic column and enter the mass spectrometer source--this must be estimated in cases where not all isomers of a given class are available). This retention time window must also include the retention time for the internal standard employed in quantifying the isomers of a particular class. Since a limited number of stable isotopically-labeled internal standards are available, the following ^{37}Cl-labeled internal standards were utilized in the present analyses to represent the CDD/CDF indicated:

i) tetra- and penta-CDD and -CDF: $^{37}Cl_4$-2,3,7,8-tetra-CDD;
ii) hexa- and hepta-CDD and -CDF: $^{37}Cl_4$-1,2,3,4,6,7,8-hepta-CDD; and
iii) octa-CDD and -CDF: $^{13}C_{12}$-octa-CDD.

4) Based on the gas chromatographic retention time data and the mass spectral data obtained as indicated above, the instrumental operating procedures listed in Table A were applied here in the analyses for tetra- through octa-chlorinated CDD/CDF.

b. Construction of Calibration Curves, Quantification. The general approach applied for quantifying CDD/CDF in each of the sample extracts was to determine the ratios of the mass spectral responses obtained for the ions characteristic of the native CDD/CDF to those of the appropriate internal standards that had been added to the sample in known concentrations prior to extraction. The concentrations of the native CDD/CDF were then determined by comparing the above data with calibration curves, prepared by plotting the analytical results obtained for a series of standards, each of which contained a fixed concentration of internal standard, but varying concentrations of

representative CDD and/or CDF. More specifically, the ratio of the ion intensity recorded for the native CDD/CDF to the ion intensity obtained for the ^{37}Cl-labelled or ^{13}C-labelled internal standard was plotted as a function of the ion intensity obtained for the internal standard. Since the internal standard was added at the beginning of the sample preparation/analysis scheme, and, as indicated in the procedures outlined above, the internal standard is quantified at the same time as the native analyte(s), it is clear that the quantitative result obtained for the internal standard reflects losses of CDD/CDF incurred during the course of sample handling and analysis. However, the internal standard may not correct for the effects of the sample matrix; that is, the added labelled internal standard may not penetrate the sample and become sorbed in the same fashion as, for example, the CDD/CDF that are incorporated in the particulates that resulted from combustion. However, the use of stable isotopically labelled internal standards as described above represents the best current approach for assessing the efficiency of the overall analytical procedure (including the extraction efficiency). In addition, as stated previously, the use of a stable isotopically labelled isomer to represent the several isomers in the same class or other classes is based on the assumption that the chemical/physical properties of the labelled isomer essentially parallel the properties of the other isomers being quantified.

Criteria which are applied in establishing that observed mass chromatographic signal responses arise from specific CDDs/CDFs are the following:

1) The mass chromatographic peaks produced by the unknown component must exhibit appropriate GC retention times; that is, they must fall within a retention time "window" established for a particular class of CDDs or CDFs (e.g., tetra-CDD). As already noted, these "windows" are established by injecting representative standards for each class of CDD and CDF.

2) Mass chromatographic peaks produced by the component must exhibit the appropriate response for at least two major ions which are known to appear in the mass spectrum of the particular CDD or CDF class being monitored. The ratio of relative intensities of the two ions monitored as indicators should correspond to that resulting from injection of an appropriate calibration standard within ± 30%.

3. In cases where the sample matrix causes shifts in the GC rentention times of the components of interest, as compared to the retention times of the corresponding standards determined from a separate injection of standards, and as indicated by analogous shifts in the retention times for the internal standards added to the sample, the identification of a specific CDD and/or CDF must be confirmed by coinjection of the sample with an added quantity of the CDD or CDF isomer in question. Enhancement of a given mass chromatographic peak upon such coinjection leads to tentative assignment of the unknown peak as a specific CDD or CDF isomer.

7. Results of Analyses forCDDs/CDFs

The quantities and concentrations (in some cases) of CDDs/CDFs which were measured in each of the combustion product and related samples analyzed in this project are listed in Table 7. Also attached to this report are copies of the mass chromatograms obtained in these analyses. For most of the analyses reported in Table 7, the recoveries of the three isotopically-labelled internal standards which were achieved were quite acceptable (generally in the 70-100% range), indicating that the analytical methodology applied is highly efficacious.

G. Other Documentation

Copies of the shipping documentation relevant to the samples analyzed in this project are provided in Appendix A of this report. Also attached in Appendix B are copies of the Brehm Laboratory Sample Tracking Forms which indicate the amount of each of the samples which was analyzed and the quantities of the isotopically-labelled internal standards which were added to the samples prior to analysis.

TABLE 1

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

VOLUMES RECEIVED AND ESTIMATED ORIGINAL VOLUMES OF LIQUID SAMPLES SUBMITTED TO THE BREHM LABORATORY FOR ANALYSES

FROM COOPER ENGINEERS EMISSIONS TESTS OF INCINERATOR FACILITY LOCATED IN TSUSHIMA, JAPAN

	SAMPLE TYPE									
	Acetone Probe And Nozzle Rinse		Toluene Probe And Nozzle Rinse		Acetone Impinger Rinse		Toluene Impinger Rinse		Impinger Liquid	
Cooper Sample Train Number	Volume Of Sample Received	Estimated Original Volume Of Sample	Volume Of Sample Received	Estimated Original Volume Of Sample	Volume Of Sample Received	Estimated Original Volume Of Sample	Volume Of Sample Received	Estimated Original Volume Of Sample	Volume Of Sample Received	Estimated Original Volume Of Sample
	Volume Received - Brehm Lab Sample Number/Volume in Milliliters; Estimated Volume in Milliliters									
2A1	CHJ-1/24	24	CHJ-34/25	36	CHJ-2/130	144	CHJ-35/79	79	CHJ-10,11/568	568
2A2	CHJ-3/22	22	CHJ-36/32	32	CHJ-4/99	104	CHJ-37/112	130	CHJ-12,13/447	447
2B1	CHJ-5/40	40	CHJ-38/61	68	CHJ-6/95	104	CHJ-39/79	79	CHJ-14/468	468
2B2	CHJ-7/102	102	CHJ-40/69	80	CHJ-8/105	105	CHJ-41/62	62	CHJ-15/454	454
2C1	CHJ-9/122	122	CHJ-42/93	102	CHJ-24/57	79	CHJ-43/116	116	CHJ-16/392	392
2C2	CHJ-25/45	80	CHJ-44/110	110	CHJ-26/116	116	CHJ-45/156	156	CHJ-17,18/514	514
2D1	CHJ-27/47	47	CHJ-46/31	43	CHJ-28/76	108	CHJ-47/112	112	CHJ-19,20/580	580
2D2	CHJ-29/86	86	CHJ-48/80	80	CHJ-30/171	171	CHJ-49/102	102	CHJ-21/432	432
2E1	CHJ-32/15	40	CHJ-51/28	59	CHJ-33/36	36	CHJ-52/47	47	CHJ-23/240 (Impinger I)	240
2E1	-	-	-	-	-	-	-	-	CHJ-22/49 (Impinger II)	49
Acetone Prewash	-	-	-	-	CHJ-31/47	66	-	-	-	-
Toluene Prewash	-	-	-	-	-	-	CHJ-50/71	71	-	-

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

WEIGHTS OF PARTICULATES COLLECTED FROM FLUE GASES IN TESTS OF INCINERATOR EFFLUENTS

AT TSUSHIMA, JAPAN FACILITY SAMPLED BY COOPER ENGINEERS

Cooper Sample Train Number	Brehm Lab Sample Number For Acetone Probe Rinse	Weight of Particulates In Acetone Rinse of Probe (grams)	Brehm Lab Sample Number For Particulate Filter	Weight of Particulates On Filter (grams)	Total Weight Of Particulates Collected By Sampling Train (grams)
2A1	CHJ-1	--[a]	CHJ-68	2.410	2.410
2A2	CHJ-3	--[a]	CHJ-69	2.540	2.540
2B1	CHJ-5	1.609	CHJ-70	0.811	2.420
2B2	CHJ-7	2.311	CHJ-71	0.660	2.971
2C1	CHJ-9	1.079	CHJ-72	0.467	1.546
2C2	CHJ-25	3.000	CHJ-73	1.534	4.534
2D1	CHJ-27	0.009	CHJ-74	0.005	0.014
2D2	CHJ-29	0.011	CHJ-75	0.008	0.019
2E1	CHJ-32	0.004	CHJ-76	0.435[b]	-

a. These samples were obtained using a Method 17 Sampling Train, in which the filter is in the stack, ahead of the probe; consequently, particulates in the acetone probe rinse were not determined in these cases. All other samples listed here were obtained using a Method 5 sampling train.

b. This weight includes the filter paper weight; a tare weight for the filter was not provided in this instance.

TABLE 3

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

WEIGHTS OF SIZED PARTICULATES COLLECTED FROM FLUE GASES USING A MULTI-CLONE SAMPLER IN TESTS OF INCINERATOR EFFLUENTS AT TSUSHIMA, JAPAN FACILITY SAMPLED BY COOPER ENGINEERS

Cooper Sample Train Number	Brehm Lab Sample Number For MF Fraction	Weight Of MF Fraction ($\lesssim 2\mu$) In Grams	Brehm Lab Sample Number For Mc IV Fraction	Weight Of Mc IV Fraction ($2 - 10\mu$) In Grams	Brehm Lab Sample Number For Mc I Fraction	Weight Of Mc I Fraction ($\lesssim 10\mu$) In Grams
3B2	CHJ-53	0.106	CHJ-55	0.038	CHJ-54	0.600
3B3	CHJ-56	0.088	CHJ-58	0.041	CHJ-57	0.423
3C2	CHJ-59	0.200	CHJ-61	0.189	CHJ-60	0.245
3C3	CHJ-62	0.117	CHJ-64	0.218	CHJ-63	0.468
3D1	CHJ-65	--[a]	CHJ-67	0.003	CHJ-66	0.002

a. Filter received had been partially burned and a portion lost; when the tare weight was deducted from the gross weight of filter received, a negative value resulted, so the particulate weight for this fraction cannot be determined.

TABLE 4

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

WEIGHTS OF RESIDUES FROM CONCENTRATION OF IMPINGER LIQUIDS TO DRYNESS - SAMPLES

OBTAINED IN TESTS OF INCINERATOR EFFLUENTS AT TSUSHIMA, JAPAN FACILITY SAMPLED BY COOPER ENGINEERS

Cooper Sample Train Number	Brehm Lab Sample Number	Total Volume of Impinger Solution (mL)	Weight of Residue From Concentration Of 50 mL of Impinger Solution (milligrams/50 mL)	Weight of Residue From Concentration Of Entire Impinger Solution (milligrams)
2A1	CHJ-10,11	568	21.0	239
2A2	CHJ-12,13	447	47.6	426
2B1	CHJ-14	468	1.2	11.2
2B2	CHJ-15	454	3.8	34.5
2C1	CHJ-16	392	3.5	27.4
2C2	CHJ-17,18	514	13.1	135
2D1	CHJ-19,20	580	1.5	17.4
2D2	CHJ-21	432	23.7	205
2D2	CHJ-22	49	--[a]	--[a]
2E1	CHJ-23	240	0.20	1.0

a. As specified, samples CHJ-21 and CHJ-22 from train 2D2 were analyzed separately for Cl^- and F^-; in this analysis, sample CHJ-22 was totally consumed and so the residue from this sample could not be determined.

TABLE 5

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

CHLORIDE AND FLUORIDE CONCENTRATIONS IN IMPINGER LIQUIDS COLLECTED IN SAMPLING FLUE GASES AT INCINERATOR FACILITY IN TSUSHIMA, JAPAN - COOPER ENGINEERS[a]

Cooper Sample Train Number	Brehm Lab Sample Number	Concentration In Impinger Liquid (μ grams/mL)		Total Volume of Impinger Liquid (mL)	Total Quantities In Impinger Liquid (m grams)	
		Chloride	Fluoride		Chloride	Fluoride
2A1	CHJ-10,11	543	1.35	568	308	0.77
2A2	CHJ-12,13	434	0.58	447	194	0.26
2B1	CHJ-14	28	0.080	468	13	0.037
2B2	CHJ-15	13	0.040	454	5.9	0.018
2C1	CHJ-16	28	0.12	392	11	0.047
2C2	CHJ-17,18	30	0.060	514	15	0.031
2D1	CHJ-19,20	11	0.61	580	6.4	0.35
2D2(1st)	CHJ-21	22	0.78	432	9.5	0.34
2D2(2nd)	CHJ-22	4.0	0.050	49	0.20	0.0025
2E1	CHJ-23	4.0	0.030	240	0.96	0.0072
2A1[b.]	CHJ-110[b.]	536	1.09	568	304	0.62
2D1[c.]	CHJ-200[c.]	10	0.49	580	5.8	0.28
-	CHJ-99[d.] (Blank)	2.0	0.020	-	-	-
-	CHJ-100[e.] (Spiked Sample)	252	1.94	-	-	-

a. These analyses accomplished by Howard Laboratories on samples prepared by Brehm Laboratory

b. This was a second aliquot of sample CHJ-10,11 which was submitted for duplicate analysis; the analytical laboratory was not aware that this was a duplicate sample.

c. This was a second aliquot of sample CHJ-19,20 which was submitted for duplicate analysis; the analytical laboratory was not aware that this was a duplicate sample.

d. This was a distilled water sample submitted in blind fashion to the analytical laboratory.

e. This was a solution prepared by the Brehm Laboratory to contain 261 μg/mL of chloride and 1.90 μg/mL of fluoride and submitted in blind fashion to the analytical laboratory.

TABLE 6

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

QUANTITIES AND CONCENTRATIONS OF SELECTED METALS IN SIZED PARTICULATES COLLECTED FROM FLUE GASES USING A MULTI-CLONE SAMPLER IN TESTS OF INCINERATOR EFFLUENTS AT TSUSHIMA, JAPAN FACILITY SAMPLED BY COOPER ENGINEERS[a].

Cooper Test Number and Fraction	Brehm Lab Sample Number	Particulate Weight in Fraction (grams)	Quantities (μ grams) and Concentrations (μ grams/gram or parts-per-million) of Metals[b].										
			As	Be	Cd	Cr	Cu	Mn	Mo	Ni	Pb	Se	Zn
3B2-MF	CHJ-53	0.106	< 2.5 (<24)	<2.0 (<19)	13 (123)	140 (1321)	116 (1094)	26 (245)	<10 (<94)	167 (1575)	230 (2170)	<2.5 (<24)	174 (1642)
3B2-Mc I	CHJ-54	0.600	3.0 (5.0)	<2.0 (<3.3)	4.0 (6.7)	131 (218)	89 (148)	213 (355)	<10 (<17)	27 (45)	134 (223)	<2.5 (<4.2)	916 (1527)
3B2-Mc IV	CHJ-55	0.038	<2.5 (<66)	<2 (<53)	3.0 (79)	13 (342)	13 (342)	16 (421)	<10 (<263)	8 (211)	50 (1316)	<2.5 (<66)	102 (2684)
3B3-MF	CHJ-56	0.088	<2.5 (<28)	<2.0 (<23)	6.0 (68)	292 (3318)	91 (1034)	36 (409)	<10 (<114)	336 (3818)	162 (1841)	<2.5 (<28)	98 (1114)
3B3-Mc I	CHJ-57	0.423	3.0 (7.1)	<2.0 (<4.7)	3.0 (7.1)	110 (260)	130 (307)	229 (541)	<10 (<24)	32 (76)	130 (307)	<2.5 (<5.9)	864 (2043)
3B3-Mc IV	CHJ-58	0.041	<2.5 (<61)	<2.0 (<49)	3.0 (73)	14 (341)	10 (244)	18 (439)	<10 (<244)	10 (244)	46 (1122)	<2.5 (<61)	88 (2146)
3C2-MF	CHJ-59	0.200	<2.5 (<13)	<2.0 (<10)	18 (90)	25 (125)	165 (825)	368 (1840)	<10 (<50)	2270 (11350)	486 (2430)	<2.5 (<13)	760 (3800)
3C2-Mc I	CHJ-60	0.245	<2.5 (<10)	<2.0 (<8.0)	2.0 (8.0)	66 (269)	51 (208)	125 (510)	<10 (<41)	25 (102)	96 (392)	<2.5 (<10)	318 (1298)
3C2-Mc IV	CHJ-61	0.189	<25 (<132)	<2.0 (<11)	6.0 (32)	19 (101)	32 (169)	32 (169)	<10 (<53)	13 (69)	90 (476)	<2.5 (<13)	278 (1471)

TABLE 6 (Continued)

Cooper Test Number and Fraction	Brehm Lab Sample Number	Particulate Weight in Fraction (grams)	Quantities (μgrams) and Concentrations (μ grams/gram or parts-per-million) of Metals[b.]										
			As	Be	Cd	Cr	Cu	Mn	Mo	Ni	Pb	Se	Zn
3C3-MF	CHJ-62	0.117	<2.5 (<21)	<2.0 (<17)	7.0 (60)	101 (863)	173 (1479)	658 (5624)	<10 (<85)	5290 (45214)	218 (1863)	<2.5 (<21)	300 (2564)
3C3-Mc I	CHJ-63	0.468	<2.5 (<5.3)	<2.0 (<4.3)	2.0 (4.3)	10 (21)	10 (21)	21 (45)	<10 (<21)	9.0 (19)	10 (21)	<2.5 (<5.3)	52 (111)
3C3-Mc IV	CHJ-64	0.218	<2.5 (<11)	<2.0 (<9.0)	3.0 (14)	14 (64)	24 (110)	30 (138)	<10 (<46)	7.0 (32)	46 (211)	<2.5 (<11)	194 (890)
3D1-MF, Mc I, Mc IV (Combined)	CHJ-65,66,67 (Combined)	--[c.]	<12	<2.0	13	46	99	55	<29	146	425	--[d.]	88
-	NBS Fly Ash, CHJ-98[e.]	0.547	10 (18)	<2.0 (<3.7)	40 (73)	46 (84)	300 (548)	406 (742)	<10 (<18)	41 (75)	3420 (6252)	15 (27)	2320 (4241)

a. These samples were analyzed by Howard Laboratories after preparation by the Brehm Laboratory.

b. The first entry under each heading is the quantity, and the concentration is given below this value in parentheses. In cases where a given element was not detected, the value cited denotes the minimum detectable quantity or concentration and is preceded by the symbol, < , (that is, less than).

c. Particulate weight could not be determined because the MF fraction filter had been partially burned and only a portion of this was provided for analysis Therefore, the concentrations could not be calculated in this case.

d. Could not be determined.

e. A sample of NBS Fly Ash, for which certified analytical data are provided by NBS, was submitted to Howard Labs in blind fashion along with the other samples listed here. The NBS certified concentrations of metals in this sample correspond to the following quantities for the sample analyzed: As 63; Be, not reported; Cd, 41; Cr, 220; Cu, 333; Mn, 470; Mo, not reported; Ni, 45; Pb, 3580; Se, not reported; Zn, 2603.

TABLE 7

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF COMBUSTION PRODUCTS COLLECTED BY COOPER ENGINEERS FROM AN INCINERATOR FACILITY IN TSUSHIMA, JAPAN FOR TETRACHLORINATED THROUGH OCTACHLORINATED DIBENZO-p-DIOXINS (CDDs) AND DIBENZOFURANS (CDFs)

Quantities in Entire Sample (nanograms) and Concentrations (nanograms per gram of sample or parts-per-billion) of CDDs/CDFs. (Concentrations Where Given are Cited in Parentheses Beneath Quantities.)[a]

Cooper Engineers Train/ Sample Number	Brehm Lab Sample Number	Sample Type	Total Tetra-CDDs	% Recovery of $^{13}C_{12}$-2,3,7,8 TCDD Internal Standard	Total Penta-CDDS	Total Hexa-CDDs	Total Hepta-CDDs	% Recovery of $^{37}Cl_4$-1,2,3,4,6,7,8-Hepta-CDD Inter. Standard	Octa-CDD	% Recovery of $^{13}C_{12}$-OCDD Internal Standard	Total Tetra-CDFs	Total Penta CDFs	Total Hexa-CDFs	Total Hepta-CDFs	Octa-CDF
2A1-17-F	CHJ-68	Filter-Trap	11ng.	75%	14ng.	8.5ng.	3.2ng.	68%	1.0ng.	68%	48ng.	21ng.	6.0ng.	1.5ng.	<0.25ng.
2A1	CHJ-1,-2, -10,-11, -34,-35	Impinger Solutions (2),Acetone & Toluene Probe & Nozzle Rinses,Acetone & Toluene Impinger Rinses Combined	31ng.	82%	28ng.	16ng.	3.6ng.	71%	1.5ng.	80%	136ng.	46ng.	10ng.	3.2ng.	1.5ng.
2A1	CHJ-78	XAD-2 Trap-Front	1.6ng.	86%	1.6ng.	1.5ng.	0.30ng.	99%	<0.30ng.	100%	6.1ng.	2.7ng.	0.70ng.	<0.20ng.	<0.30ng.
2A2-17-F	CHJ-69	Filter-Trap	5.1ng.	74%	4.6ng.	3.6ng.	2.0ng.	78%	0.060ng.	75%	52ng.	27ng.	6.8ng.	1.5ng.	<0.050ng.
2A2	CHJ-3,-4, -12,-13, -36,-37	Impinger Solutions (2),Acetone & Toluene Probe & Nozzle Rinses,Acetone & Toluene Impinger Rinses Combined	63ng.	93%	35ng.	18ng.	7.0ng.	100%	2.2ng.	99%	980ng.	260ng.	42ng.	9.8ng.	1.0ng.
2A2	CHJ-79	XAD-2 Trap-Front	21ng.	74%	3.8ng.	5.0ng.	3.5ng.	60%	1.0ng.	60%	324ng.	84ng.	9.0ng.	<1.0ng.	<1.0ng.
2A2	CHJ-80	XAD-2 Trap-Back	4.4ng.	84%	1.3ng.	2.6ng.	0.80ng.	40%	<0.70ng.	42%	71ng.	28ng.	1.8ng.	<0.5ng.	<0.50mg.
2B1-M5-F	CHJ-38,-70	Particulate Filter, Toluene Probe and Nozzle Rinse Combined	4.1ng. (5.0ppb)	82%	5.2ng. (6.4ppb)	6.7ng. (8.3ppb)	2.4ng. (2.9ppb)	83%	1.5ng. (1.8ppb)	90%	14ng. (17ppb)	6.9ng. (8.5ppb)	2.8ng. (3.5ppb)	1.2ng. (1.5ppb)	<0.24ng. (<0.30ppb)
2B1	CHJ-5	Acetone Probe & Nozzle Rinse	3.3ng.	84%	3.0ng.	<1.0ng.	2.0ng.	78%	<1.0ng.	72%	8.3ng.	4.9ng.	<1.0ng.	<0.50ng.	<1.0ng.
2B1	CHJ-81	XAD-2 Trap-Front	7.8ng.	78%	1.2ng.	0.50ng.	<0.50ng.	62%	<0.50ng.	65%	20ng.	5.1ng.	<0.15ng.	<2.5ng.	<0.50ng.
2B1	CHJ-6,-14, -39	Impinger Solutions (2),Acetone & Toluene Impinger Rinses Combined	44ng.	84%	45ng.	26ng.	4.1ng.	84%	1.5ng.	92%	139ng.	86ng.	12ng.	2.1ng.	<0.50ng.

TABLE 7 - (Continued)

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF COMBUSTION PRODUCTS COLLECTED BY COOPER ENGINEERS FROM AN INCINERATOR FACILITY IN TSUSHIMA, JAPAN FOR TETRACHLORINATED THROUGH OCTACHLORINATED DIBENZO-p-DIOXINS (CDDs) AND DIBENZOFURANS (CDFs)

Quantities in Entire Sample (nanograms) and Concentrations (nanograms per gram of sample or parts-per-billion) of CDDs/CDFs. (Concentrations Where Given are Cited in Parentheses Beneath Quantities.)[a]

Cooper Engineers Train/ Sample Number	Brehm Lab Sample Number	Sample Type	Total Tetra-CDDs	% Recovery of $^{13}C_{12}$-2,3,7,8 TCDD Internal Standard	Total Penta-CDDS	Total Hexa-CDDs	Total Hepta-CDDs	% Recovery of $^{37}Cl_4$-1,2,3,4,6,7,8-Hepta-CDD Inter. Standard	Octa-CDD	% Recovery of $^{13}C_{12}$-OCDD Internal Standard	Total Tetra-CDFs	Total Penta CDFs	Total Hexa-CDFs	Total Hepta-CDFs	Octa-CDF
2B2-M5-F	CHJ-40,-71	Particulate Filter,Toluene Probe & Nozzle Rinse Combined	1.5ng. (2.2ppb)	80%	1.5ng. (2.2ppb)	0.99ng. (1.5ppb)	1.2ng. (1.8ppb)	64%	1.3ng. (1.9ppb)	71%	17ng. (25ppb)	8.6ng. (13ppb)	1.5ng. (2.3ppb)	1.4ng. (2.1ppb)	0.92ng. (1.4ppb)
2B2	CHJ-7	Acetone Probe & Nozzle Rinse	4.9ng.	94%	3.4ng.	3.3ng.	2.2ng.	88%	<1.5ng.	100%	48ng.	17ng.	4.8ng.	1.3ng.	<1.5ng.
2B2	CHJ-83	XAD-2 Trap-Front	5.8ng.	86%	1.4ng.	0.30ng.	<0.30ng.	82%	<0.40ng.	100%	81ng.	14ng.	1.2ng.	<0.20ng.	<0.40ng.
2B2	CHJ-8, -15,-41	Impinger Solutions, (2),Acetone & Toluene Impinger Rinses Combined	124ng.	88%	75ng.	28ng.	11ng.	100%	2.2ng.	91%	1443ng.	598ng.	75ng.	7.0ng.	<1.0ng.
2C1-M5-F	CHJ-42,-72	Particulate Filter, Toluene Probe & Nozzle Rinse Combined	1.5ng. (3.3ppb)	81%	3.3ng. (7.0ppb)	5.1ng. (11ppb)	1.6ng. (3.5ppb)	85%	1.6ng. (3.4ppb)	100%	4.2ng. (8.9ppb)	2.4ng. (5.2ppb)	1.2ng. (2.6ppb)	1.3ng. (2.7ppb)	1.1ng. (2.4ppb)
2C1	CHJ-9	Acetone Probe & Nozzle Rinse	2.7ng.	85%	4.5ng.	5.0ng.	1.0ng.	100%	2.0ng.	99%	6.1ng.	6.5ng.	2.1ng.	1.0ng.	<1.0ng.
2C1	CHJ-85	XAD-2 Trap-Front	0.80ng.	68%	<0.20ng.	<0.15ng.	<0.30ng.	100%	<0.40ng.	100%	3.2ng.	<0.20ng.	<0.10ng.	<0.30ng.	<0.40ng.
2C1	CHJ-16,-24, -43	Impinger Solutions (2),Acetone & Toluene Impinger Rinses Combined	21ng.	67%	13ng.	5.2ng.	1.0ng.	55%	2.9ng.	60%	76ng.	25ng.	2.7ng.	1.9ng.	2.5ng.
2C2-M5-F	CHJ-44,-73	Particulate Filter, Toluene Probe & Nozzle Rinse Combined	13ng. (8.8ppb)	69%	12ng. (7.7ppb)	10ng. (6.6ppb)	3.1ng. (2.0ppb)	64%	0.92ng. (0.60ppb)	54%	98ng. (64ppb)	61ng. (40ppb)	14ng. (9.0ppb)	2.6ng. (1.7ppb)	<0.77ng. (<0.50ppb)
2C2	CHJ-25	Acetone Probe & Nozzle Rinse	2.7ng.	90%	<1.0ng.	1.3ng.	<1.0ng.	92%	<2.0ng.	90%	32ng.	19ng.	2.7ng.	<1.0ng.	<2.0ng.

TABLE 7 - (Continued)

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF COMBUSTION PRODUCTS COLLECTED BY COOPER ENGINEERS FROM AN INCINERATOR FACILITY IN TSUSHIMA, JAPAN FOR TETRACHLORINATED THROUGH OCTACHLORINATED DIBENZO-p-DIOXINS (CDDs) AND DIBENZOFURANS (CDFs)

Quantities in Entire Sample (nanograms) and Concentrations (nanograms per gram of sample or parts-per-billion) of CDDs/CDFs. (Concentrations Where Given are Cited in Parentheses Beneath Quantities.)[a]

Cooper Engineers Train/ Sample Number	Brehm Lab Sample Number	Sample Type	Total Tetra-CDDs	% Recovery of $^{13}C_{12}$-2,3,7,8 TCDD Internal Standard	Total Penta-CDDS	Total Hexa-CDDs	Total Hepta-CDDs	% Recovery of $^{37}Cl_4$-1,2,3,4,6,7,8-Hepta-CDD Inter. Standard	Octa-CDD	% Recovery of $^{13}C_{12}$-OCDD Internal Standard	Total Tetra-CDFs	Total Penta CDFs	Total Hexa-CDFs	Total Hepta-CDFs	Octa-CDF
2C2	CHJ-87	XAD-2 Trap-Front	13ng.	82%	2.8ng.	0.60ng.	<0.30ng.	86%	<0.30ng.	87%	160ng.	22ng.	1.4ng.	<0.30ng.	<0.30ng.
2C2	CHJ-17,-18, -26, -45	Impinger Solutions (2),Acetone & Toluene Impinger Rinses Combined	67ng.	75%	49ng.	9.3ng.	2.0ng.	85%	<1.0ng.	72%	760ng.	259ng.	21ng.	1.8ng.	<0.50ng.
2D1	CHJ-46,-74	Particulate Filter, Toluene Probe & Nozzle Rinse Combined	<0.035ng. (<7.0ppb)	57%	<0.055ng. (<11ppb)	<0.12ng. (<23ppb)	<0.15ng. (<30ppb)	49%	<0.75ng. (<150ppb)	40%	<0.035ng. (<7.0ppb)	<0.065ng. (<13ppb)	<0.10ng. (<20ppb)	<0.25ng. (<50ppb)	<0.75ng. (<150ppb.
2D1	CHJ-27	Acetone Probe & Nozzle Rinse	0.080ng.	76%	0.50ng.	0.90ng.	0.40ng.	100%	0.20ng.	100%	<0.050ng.	<0.060ng.	<0.080ng	<0.15ng.	<0.15ng.
2D1	CHJ-89	XAD-2 Trap-Front	7.1ng.	79%	1.3ng.	<0.50ng.	<0.30ng.	98%	<0.30ng.	99%	9.2ng.	<0.30ng.	<0.30ng.	<0.30ng.	<0.30ng.
2D1	CHJ-19,-20, -28,-47	Impinger Solutions (2),Acetone & Toluene Impinger Rinses Combined	396ng.	73%	222ng.	103ng.	10ng.	63%	8.3ng.	66%	185ng.	89ng.	15ng.	2.5ng.	<1.0ng.
2D2-M5-F	CHJ-48,-75	Particulate Filter, Toluene Probe & Nozzle Rinse Combined	1.1ng (132ppb)	80%	2.1ng. (266ppb)	37ng. (4570ppb)	1.0ng. (128ppb)	77%	1.3ng. (160ppb)	77%	4.7ng. (587ppb)	2.6ng. (328ppb)	0.88ng. (110ppb)	0.42ng. (53ppb)	0.80ng. (100ppb)
2D2	CHJ-29	Acetone Probe & Nozzle Rinse	8.8ng.	100%	15ng.	22ng.	7.0ng.	100%	4.9ng.	100%	28ng.	20ng.	1.2ng.	1.4ng.	<0.50ng.
2D2	CHJ-91	XAD-2 Trap-Front	4.6ng.	88%	2.6ng.	2.6ng.	0.30ng.	81%	<0.50ng.	83%	14ng.	2.0ng.	0.30ng.	<0.20ng.	<0.30ng.
2D2	CHJ-21,-30, -49	First Impinger Solution,Acetone& Toluene Impinger Rinses Combined	275ng.	95%	305ng.	261ng.	70ng.	100%	28ng.	95%	1188ng.	414ng.	55ng.	11ng.	2.5ng.

TABLE 7 - (Continued)

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF COMBUSTION PRODUCTS COLLECTED BY COOPER ENGINEERS FROM AN INCINERATOR FACILITY IN TSUSHIMA, JAPAN FOR TETRACHLORINATED THROUGH OCTACHLORINATED DIBENZO-p-DIOXINS (CDDs) AND DIBENZOFURANS (CDFs)

Quantities in Entire Sample (nanograms) and Concentrations (nanograms per gram of sample or parts-per-billion) of CDDs/CDFs. (Concentrations Where Given are Cited in Parentheses Beneath Quantities.)[a]

Cooper Engineers Train/ Sample Number	Brehm Lab Sample Number	Sample Type	Total Tetra-CDDs	% Recovery of $^{13}C_{12}$-2,3,7,8 TCDD Internal Standard	Total Penta-CDDS	Total Hexa-CDDs	Total Hepta-CDDs	% Recovery of $^{37}Cl_4$-1,2,3,4,6,7,8-Hepta-CDD Inter. Standard	Octa-CDD	% Recovery of $^{13}C_{12}$-OCDD Internal Standard	Total Tetra-CDFs	Total Penta CDFs	Total Hexa-CDFs	Total Hepta-CDFs	Octa-CDF
2D2	CHJ-22	Third Impinger (yellow)	0.60ng.	68%	<0.50ng.	0.60ng.	<1.0ng.	61%	<1.0ng.	60%	1.0ng.	<0.50ng.	<0.50ng.	<1.0ng.	<1.0ng.
2E1-M5-F	CHJ-51,-76	Particulate Filter, Toluene Probe & Nozzle Rinse Combined	<0.35ng.	85%	<0.15ng.	<0.66ng.	0.44ng.	100%	1.3ng.	100%	<0.26ng.	<0.22ng.	<0.40ng.	1.3ng.	1.5ng.
2E1	CHJ-32	Acetone Probe & Nozzle Rinse	<0.050ng.	95%	<0.10ng.	<0.25ng.	1.4ng.	100%	3.0ng.	100%	<0.050ng.	<0.10ng.	<0.20ng.	1.2ng.	0.80ng.
2E1	CHJ-93	XAD-2 Trap-Front	<0.10ng.	72%	<0.15ng.	<0.20ng.	<0.30ng.	62%	<0.50ng.	56%	<0.10ng.	<0.15ng.	<0.15ng.	<0.40ng.	<0.50ng.
2E1	CHT-23, -33,-52	Impinger Water, Acetone & Toluene Impinger Rinses Combined	<0.20ng.	15%	<0.50ng.	<0.80ng.	<0.50ng.	11%	<1.5ng.	13%	<0.20ng.	<0.50ng.	<0.80ng.	<0.70ng.	<1.5ng.
2D	CHJ-31	Acetone Prewash	<0.050ng.	100%	<0.070ng.	<0.16ng.	0.40ng.	100%	1.4ng.	100%	<0.050ng.	<0.070ng.	<0.070ng.	0.40ng.	0.40ng.
2D	CHJ-50	Toluene Prewash	<0.050ng.	95%	<0.050ng.	<0.080ng.	<0.13ng.	83%	0.50ng.	92%	<0.050ng.	<0.050ng.	<0.090ng.	0.40ng.	0.40ng.
2A4	CHJ-95	Knock-out Fly Ash/NA Combined DS/FF-10/14/83,JLH,WM, HI	28ppb	67%	29ppb	27ppb	1.6ppb	100%	<0.70ppb	100%	5.4ppb	3.8ppb	1.3ppb	0.40ppb	<0.50ppb.
2B3	CHJ-96	Dry Scrubber Fly Ash-10/14/83, JLH,WM,HI	0.40ppb	62%	<0.15ppb	<0.20ppb.	<0.20ppb.	51%	<0.50ppb.	35%	<0.10ppb.	<0.10ppb.	<0.10ppb.	<0.15ppb.	<0.50ppb.
2D4	CHJ-97	FF Fly Ash-10/14/83,JLH,WM,HI	20ppb.	93%	9.5ppb.	9.0ppb.	1.5ppb.	71%	<0.70ppb.	70%	7.5ppb.	1.9ppb.	0.60ppb.	0.20ppb.	<0.50ppb.

TABLE 7 - (Continued)

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF COMBUSTION PRODUCTS COLLECTED BY COOPER ENGINEERS FROM AN INCINERATOR FACILITY IN TSUSHIMA, JAPAN FOR TETRACHLORINATED THROUGH OCTACHLORINATED DIBENZO-p-DIOXINS (CDDs) AND DIBENZOFURANS (CDFs)

Quantities in Entire Sample (nanograms) and Concentrations (nanograms per gram of sample or parts-per-billion) of CDDs/CDFs. (Concentrations Where Given are Cited in Parentheses Beneath Quantities.)[a]

Cooper Engineers Train/ Sample Number	Brehm Lab Sample Number	Sample Type	Total Tetra-CDDs	% Recovery of $^{13}C_{12}$-2,3,7,8 TCDD Internal Standard	Total Penta-CDDS	Total Hexa-CDDs	Total Hepta-CDDs	% Recovery of $^{37}Cl_4$-1,2,3,4,6,7,8-Hepta-CDD Inter. Standard	Octa-CDD	% Recovery of $^{13}C_{12}$-OCDD Internal Standard	Total Tetra-CDFs	Total Penta CDFs	Total Hexa-CDFs	Total Hepta-CDFs	Octa-CDF
3B2 MF	CHJ-53	Multi-clone (<2.8μ)	<1.0ppb	86%	<0.80ppb	<2.0ppb	2.2ppb	92%	<2.0ppb	100%	<1.0ppb	<2.0ppb	<1.5ppb	<1.0ppb	<2.0ppb
3B2 Mc IV	CHJ-55	Multi-clone (2.8-12.7μ)	4.5ppb	77%	<2.0ppb	<7.0ppb	3.3ppb	100%	<4.0ppb	100%	5.8ppb	<2.5ppb	<2.0ppb	<2.0ppb	<4.0ppb
3B2 Mc I	CHJ-54	Multi-clone (>12.7μ)	1.5ppb	78%	0.60ppb	<0.35ppb	<0.50ppb	55%	<0.40ppb	57%	2.5ppb	0.70ppb	<0.15ppb	<0.40ppb	<0.50ppb
3B3 MF	CHJ-56	Multi-clone (<2.7μ)	<1.0ppb	95%	<1.0ppb	<1.5ppb	1.1ppb	100%	<2.5ppb	100%	<1.0ppb	<2.5ppb	<1.5ppb	<1.0ppb	<2.0ppb
3B3 Mc IV	CHJ-58	Multi-clone (2.7-12.5μ)	<5.0ppb	91%	<7.0ppb	<25ppb	<5.0ppb	100%	<7.0ppb	100%	<5.0ppb	<10ppb	<10ppb	<5.0ppb	<6.0ppb
3B3 Mc I	CHJ-57	Multi-clone (>12.5μ)	44ppb	38%	24ppb	11ppb	1.0ppb	46%	<1.0ppb	56%	<0.50ppb	<0.50ppb	<0.80ppb	<0.50ppb	<1.0ppb
3C2 MF	CHJ-59	Multi-clone (<2.2μ)	<0.30ppb	86%	<0.50ppb	<1.0ppb	0.50ppb	100%	<1.0ppb	100%	<0.50ppb	<0.70ppb	<0.50ppb	<0.50ppb	<1.0ppb
3C2 Mc IV	CHJ-61	Multi-clone (2.2-11.1μ)	<0.70ppb	80%	<0.40ppb	<1.0ppb	<0.40ppb	87%	<1.0ppb	81%	<0.50ppb	<1.0ppb	<0.50ppb	<0.50ppb	<1.0ppb
3C2 Mc I	CHJ-60	Multi-clone (>11.1μ)	1.5ppb	81%	1.0ppb	1.0ppb	<0.50ppb	71%	1.0ppb	77%	<0.50ppb	<0.80ppb	<0.60ppb	<0.50ppb	<0.90ppb
3C3 MF	CHJ-62	Multi-clone (<2.4μ)	<0.70ppb	71%	<1.5ppb	<2.5ppb	<2.5ppb	91%	<4.0ppb	80%	<1.0ppb	<1.5ppb	<2.5ppb	<3.0ppb	<4.0ppb
3C3 Mc IV	CHJ-64	Multi-clone (2.4-11.6μ)	<0.30ppb	79%	2.0ppb	1.0ppb	<0.50ppb	81%	<0.50ppb	89%	<0.30ppb	<0.70ppb	<0.50ppb	<0.30ppb	<0.50pp
3C3 Mc I	CGJ-63	Multi-clone (>11.6μ)	16ppb	42%	7.5ppb	6.5ppb	<1.0ppb	80%	<1.5ppb	60%	<1.0ppb	<1.5ppb	<1.5ppb	<2.0ppb	<1.5ppb
3D1 MF, McI, Mc IV Combined	CHJ-65, -66, -67	Multi-clone (All Three Fractions)	<50pg.	52%	<60pg.	<150pg.	<150pg.	68%	<350pg.	80%	<50pg.	<50pg.	<150pg.	<120pg.	<200pg.

a. The notation, "<-", indicates that no CDDs or CDFs were detected in excess of the Minimum Detectable Quantity or concentration which is given following the "<-" notation.

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STANDARD PROTOCOL FOR RECORDING FURNACE OPERATING DATA DURING SAMPLING FOR TRACE EMISSIONS OF CHLORINATED ORGANIC COMPOUNDS IN ENERGY FROM SOLID WASTE COMBUSTION PLANTS

INTRODUCTION

The information on furnace operation which should be gathered during tests for trace emissions of chlorinated organic compounds is summarized in the following data form. It will be noted that actual values while sampling is underway in the form of copies of actual strip charts is the preferable form of reporting operating information.

Where design information is requested, it should be characteristic of normal operation at the time of year when sampling is actually being done. Comparison between the expected and actual values during sampling is a guide as to whether the system was operating normally while it was being sampled. If the comparison suggests the system may not have been operating normally during sampling, it may be difficult to utilized the data.

It will also be noted that some of the required information is to be collected as nearly continuously as possible during sampling. This is so as to permit detection of changes, intended and inadvertent, which may have occurred during sampling. The occurrence or absence of any such changes is a factor in interpreting the results of the sampling.

Recording the essential information shall begin at least three hours before sampling is begun and be continued for at least an hour after sampling is terminated.

The following form is intended to accompany reports on source sampling at refuse-to-energy facilities.

BACKGROUND INFORMATION

1. Name and address of the facility: _____

   _____

   _____

2. Name and telephone number of plant general manager or other person to contact regarding emission sampling program:

   _____ # _____

3. Name and telephone number of emission sampling team manager:

   _____ # _____

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4. Name and telephone number of person responsible for laboratory analysis of samples:

_____ # _____

5. Name and telephone number of meteorological monitoring station servicing the locality of the plant:

_____ # _____

6. Designation of the combustion train actually sampled:

_____ # _____

7. Date of emission sampling: _____

Time when sampling started: _____

Time when sampling terminated: _____

FACILITY DESCRIPTION

8. Type of refuse processing system (e.g., mass-burn, refuse derived fuel):

_____

9. Describe refuse preparation method, if appropriate: _____

_____

10. Type of furnace (e.g., waterwall, refractory-wall, hybrid): _____

_____

Is auxiliary fuel regularly fired? If so, what fuel? _____

11. Design heat release rate (MMBtu/hr): _____

12. Design steam production rate and conditions: _____ lbs/hr @ _____ °F, _____ psig, and (if saturated) _____ % quality.

13. Feed properties for which unit was designed:

- Range of heating values _____ to _____ Btu/lb
- Range of moisture contents _____ to _____ wt %
- Range of ash contents _____ to _____ wt %

14. Please provide a cross-sectional diagram of the facility, preferably to scale, showing the spatial relationship between the major elements of the process train, including: the waste feed system to the grate; the grate

and residue removal system; shape of the furnace; primary and secondary combustion air ports; the boiler and its flue gas passages; soot blowers; major heat transfer surfaces; economizer; air preheater (if appropriate); air pollution control system; induced draft fan; and stack. Indicate locations of temperature and pressure detectors also.

15. Description of the grate system:

- Supplier: _____
- Type (e.g., reciprocating, roller, traveling, rotary): _____
- Number of step sections (if appropriate): _____
- Grate area (ft^2) (or equivalent): _____

16. Description of the boiler:

- Supplier: _____
- Furnace volume (ft^3): _____
- Firebox dimensions (ft): L _____ W _____ H _____
- Kind of soot blowers: _____
- Soot blowing schedule (approximate times): _____

17. Type of combustion (e.g., excess air, starved air): _____

_____

18. Overfire and underfire air distribution:

- Describe design and type of all air ports: _____

_____

_____

- Describe how total combustion air and air distribution is controlled

_____

_____

- Verify that air distribution systems are operating as designed:

_____

_____

19. Type of draft: _____

How is draft regulated: _____

20. Description of solid waste feeding and stoking system:

- How is feeding rate controlled? _____
- Frequency and length of feed ram stroke: _____

21. Describe the overall plant control system logic (e.g., what measurements are used as the basis for controlling firing rate?): _____

_____

22. Stack height (ft): _____

Stack diameter at top (ft): _____

23. Type of air pollution control system: _____

24. If electrostatic precipitator:

- Specific collection area (ft^2/1000 ACFM): _____
- Design temperature at inlet (°F): _____
- Number of independent bus sections: _____
- Which independent bus sections were in service during emission sampling? _____
- Design particulate loading at inlet: _____ grains/dscf

at outlet: _____ grains/dscf

Rapping frequency: _____

25. If fabric filter:

- Fabric type _____ Weight _____ Weave _____ Finish _____
- Bag cleaning method and frequency: _____

_____

- Air-to-cloth ratio (ACFM/ft^2): _____
- Design pressure drop across bags (in., W.G.): _____
- Design gas temperature at inlet (°F): _____
- Total number of bags: _____

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- Actual number of bags in service at time of sampling: _____

- Range in pressure drop across bags during testing: _____

26. Which flue gas components are regularly measured? Indicate location of monitor:

	Instrument Model	Location	Unit Served by This Monitor
Oxygen	_____	_____	_____
Carbon Monoxide	_____	_____	_____
Hydrocarbons	_____	_____	_____
Other (Specify)	_____	_____	_____

Is flue gas opacity regularly monitored? _____

27. Description of existing temperature monitors:

Locations: _____

Type of temperature detector(s): _____

Manufacturer and model number: _____

Date of most recent calibration: _____

28. Time constants of in-plant measuring devices (pressure gauges, flue gas monitors, thermocouples): _____

29. What is the voluntary shutdown schedule for routine maintenance of the process train being sampled? _____

Dates of the most recent shutdown for routine maintenance and type of maintenance performed? _____

30. Types of refuse normally accepted at the facility (please indicate source of this information):

	Approximate Percentage
Residential	_____
Commercial/Institutional	_____
Industrial	_____

Construction debris _____

Known hazardous waste _____

TEST DATA

31. Barometric pressure at start of test (in. Hg): _____

32. Precipitation over seven days prior to test (in.) by day: _____

33. Relative humidity at start of test: _____

34. Temperature of combustion air after any air heaters (°F):

Underfire _____ Overfire _____

35. Temperatures of combustion air at inlets to forced draft fan (°F):

Underfire _____ Overfire _____

36. Combustion air flow rates (ACFM preferable) or pressure if flow is not available - include strip chart record if available or record measurements on indicators at 15 minute intervals at a minimum:

Underfire _____ Overfire _____

37. Solid waste firing rate over test period (attach strip chart record if available; if not available, give total quantity of waste fired over sampling period and maximum and minimum firing rates): _____

_____

Indicate method of determining firing rate [load cell, crane count, ram cycle, other (specify)]: _____

_____

38. Auxiliary fuel firing rate over test period (attach strip chart record if available; if not available, give total quantity of waste fired over sampling period and maximum and minimum firing rates): _____

_____

39. If soot blowing occurs during sampling period, give times and duration:

_____

40. Furnace temperatures:

- Design temperatures and locations: _____°F, _____
- Attach summary record of furnace temperature measurements during corresponding month of past years

- Attach strip chart record of temperature at top of furnace, in front of screen tubes - over the sampling period (if records are available for more than one in-plant thermocouple, include them and specify their locations)

41. Flue gas analysis:

- Attach strip chart records for concentrations of the following flue gas constituents, measured over the sampling period: carbon monoxide, carbon dioxide, oxygen, nitrogen oxide, sulfur dioxide, total hydrocarbons, water vapor, and flue gas flow

- Attach strip chart record for in-stack opacity over the sampling

42. Include a copy of the operator's log for the period of the test.

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SAMPLING FOR THE DETERMINATION OF CHLORINATED ORGANIC COMPOUNDS IN STACK EMISSIONS

1. PRINCIPLE AND APPLICABILITY

1.1 Principle: Stack gases that may contain chlorinated organic compounds are withdrawn from the stack using a sampling train. The analyte is collected in the sampling train. The compounds of interest are determined by solvent extraction followed by gas chromatography/mass spectroscopy (GC/MS).

1.2 Applicability: This method is applicable for the determination of chlorinated organic compounds in stack emissions. The sampling train is so designed that only the total amount of each chlorinated organic compound in the stack emissions may be determined. To date, no studies have been performed to demonstrate that the particulate and/or gaseous chlorinated organic compounds collected in separate parts of the sampling train accurately describes the actual partition of each in the stack emissions. If separate parts of the sampling train are analyzed separately, the data should be included and so noted as in Section 2 below. The sampling shall be conducted by competent personnel experienced with this test procedure and cognizant of intricacies of the operation of the prescribed sampling train and constraints of the analytical techniques for chlorinated organic compounds, especially PCDDs and PCDFs.

Note: This method assumes that all of the compounds of interest are collected either on the XAD-2 resin or in upstream sampling train components. Since the method at the present time has not been validated in the presence of all the other components present (HCl, high organic load) in the stack emission, it is recommended that appropriate quality control (QC) steps be employed until such validation has been completed. These QC steps may include the use of a backup resin trap or the addition of a representative labeled standard (distinguishable from the internal standard used for quantitation) to the filter and/or the XAD-2 in the field prior to the start of sampling. These steps will provide information on possible breakthrough of the compounds of interest.

2. REPORTABILITY

Recognizing that modification of the method may be required for specific applications, the final report of a test where changes are made shall include: (1) the exact modification; (2) the rationale for the modification; and (3) an estimate of the effect the modification will produce on the data.

3. RANGE OF MINIMUM DETECTABLE STACK GAS CONCENTRATION

The range of the analytical method may be expanded considerably through concentration and/or dilution. The total method sensitivity is also highly dependent on the volume of stack gas sampled and the detection limit of the analytical finish. The user shall determine for their system the minimum detectable stack gas concentration for the chlorinated organic compounds of interest. The minimum detectable stack gas concentration should generally be in the ng/m^3 (nanogram/cubic meter) or lower range.

4. INTERFERENCES

Organic compounds other than the compounds of interest may interfere with the analysis. Appropriate sample clean-up steps shall be performed. Through all stages of sample handling and analysis, care should be taken to avoid contact of samples and extracts with synthetic organic materials other than polytetrafluorethylene (TFE®). Adhesives should not be used to hold TFE® liners on lids (but, if necessary, appropriate blanks must be run), and lubricating and sealing greases must not be used on the sampling train.

5. PRECISION AND ACCURACY

Precision and accuracy measurements have not yet been made on PCDD and PCDF using this method. These measurements are needed. However, recovery efficiencies for source samples spiked with compounds have ranged from 70 to 120%.[1,5]

6. SAMPLING RUNS, TIME, AND VOLUME

6.1 Sampling Runs: The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3).

6.2 Sampling Time: The sampling time must be of sufficient length to provide coverage of the average operating conditions of the source. However, this shall not be less than three hours (3).

6.3 Sample Volume: The sampling volume must be sufficient to provide the required amount of analyte to meet both the MDL of the analytical finish and the allowable stack emissions. It may be calculated using the following formula:

$$\text{Sample Volume} = A \times \frac{100}{B} \times \frac{100}{C} \times \frac{1}{D}$$

A = The analytical MDL in ng
B = Percent (%) of the sample required per analytical finish run

C = The sample recovery (%)
D = The allowable stack emissions (ng/m^3)

Example: A = 0.050 ng; B = 10%; C = 50%; and D = 1 ng/m^3

$$SV = 0.05 \times \frac{100}{10} \times \frac{100}{50} \times \frac{1}{1} = 1m^3$$

7. APPARATUS

Sampling Train: The train consists of nozzle, probe, heated particulate filter, and sorbent module followed by four impingers (Fig. 1). Provision is made for the addition of (1) a cyclone in the heated filter box when testing sources emitting high concentrations of particulate matter, (2) a large water trap between the heated filter and the sorbent module for stack gases with high moisture content, and (3) additional impingers following the sorbent module. If one of the options is utilized, the option used shall be detailed in the report. The train may be constructed by adaption of an EPA Method 5 train. Descriptions of the sampling train components are contained in the following sections.

7.1.1 Nozzle

The nozzle shall be made to the specifications of EPA Method 5. The nozzle may be made of nickel plated stainless steel, quartz, or borosilicate glass.

7.1.2 Probe

The probe shall be lined or made of TFE®, borosilicate, or quartz glass. The liner or probe extends past the retaining nut into the stack. A temperature controlled jacket provides protection of the liner or probe. The liner or probe shall be equipped with a connecting fitting that is capable of forming a leak-free, vacuum-tight connection without sealing greases.

7.1.3 Sample Transfer Lines (optional)

The sample transfer lines, if needed, shall be heat traced, heavy walled TFE® (1.3 cm [1/2 in.] O.D. x 0.3 cm [1/8 in.] wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line should be as short as possible and must be maintained at 120°C.

7.1.4 Filter Holder

Borosilicate glass, with a glass frit filter support and a glass-to-glass seal or TFE® gasket. A rubber gasket shall not be used. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

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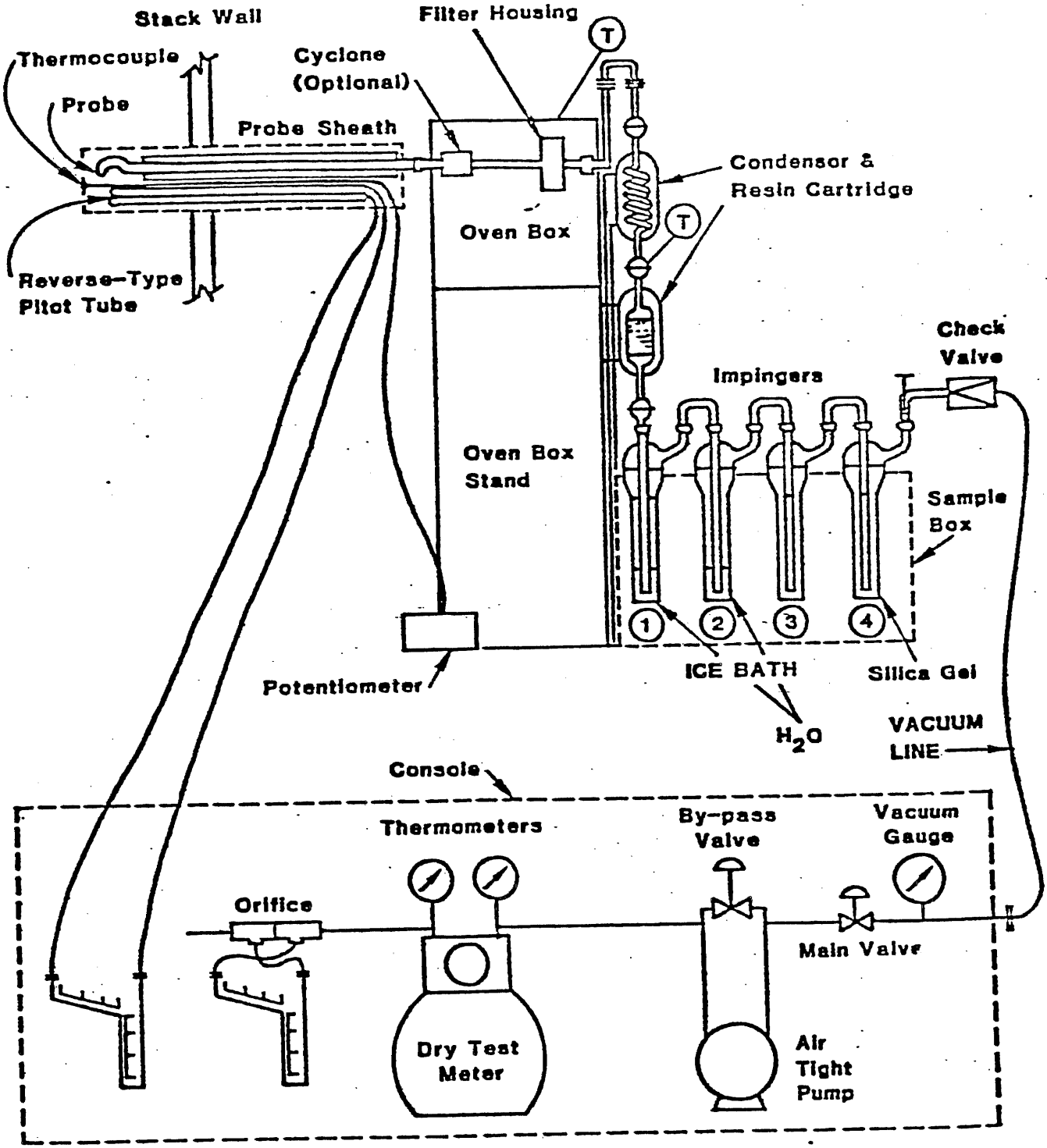

Impingers are of the Modified Greenberg-Smith Type

Impingers 1 and 2 Contain 100 ml Water

Impinger 3 Empty

Impinger 4 Contains 200-300 Grams Silica Gel

Impinger 1 is the Hexane-Rinsed Back-Up to the Resin Cartridge

(T) = Thermocouple location

Fig. 1. Modified EPA Method 5 Train for Organics Sampling

Source: Methods Manual Sampling and Analysis Procedures for Assessing Organics Emissior from Stationary Combustion Sources in Exposure Evaluation Division Studies, U.S. Environmental Protection Agency Report No. EPA-560-82-014 (January 1982).

7.1.5 Cyclone in Filter Box (optional)

The cyclone shall be constructed of borosilicate glass with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases.

7.1.6 Filter Heating System

The heating system must be capable of maintaining a temperature around the filter holder (and cyclone, if used) during sampling of 120±14°C (248±25°F). A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling.

7.1.7 Solid Sorbent Module

Amberlite XAD-2® resin (XAD-2), confined in a trap, shall be used as the sorbent. The sorbent module shall be made of glass with connecting fittings that are able to form leak-free, vacuum-tight seals without use of sealant greases (Figs. 2 and 3). The XAD-2 trap must be in a vertical position. It is preceded by a coil-type condenser, also oriented vertically, with circulating cold water. Gas entering the sorbent module must be maintained at ≤20°C (68°F). Gas temperature shall be monitored by a thermocouple placed either at the inlet or exit of the sorbent trap. The sorbent bed must be firmly packed and secured in place to prevent settling or channeling during sample collection. Ground glass caps (or equivalent) must be provided to seal the sorbent-filled trap both prior to and following sampling. All sorbent modules must be maintained in the vertical position during sampling.

7.1.8 Impingers

Four or more impingers with connecting fittings able to form leak-free, vacuum-tight seals without sealant greases when connected together, shall be used. All impingers are of the Greenburg-Smith design modified by replacing the tip with 1.3 cm (1/2 in.) ID glass tube extending to 1.3 cm (1/2 in.) from the bottom of the flask.

7.1.9 Metering System

The metering system shall consist of a vacuum gauge, a leak-free pump, thermometers capable of measuring temperature to within 3°C (~5°F), a dry gas meter with 2 percent accuracy at the required sampling rate, and related equipment, or equivalent.

7.1.10 Barometer

Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 Hg (0.1 in. Hg) shall be used.

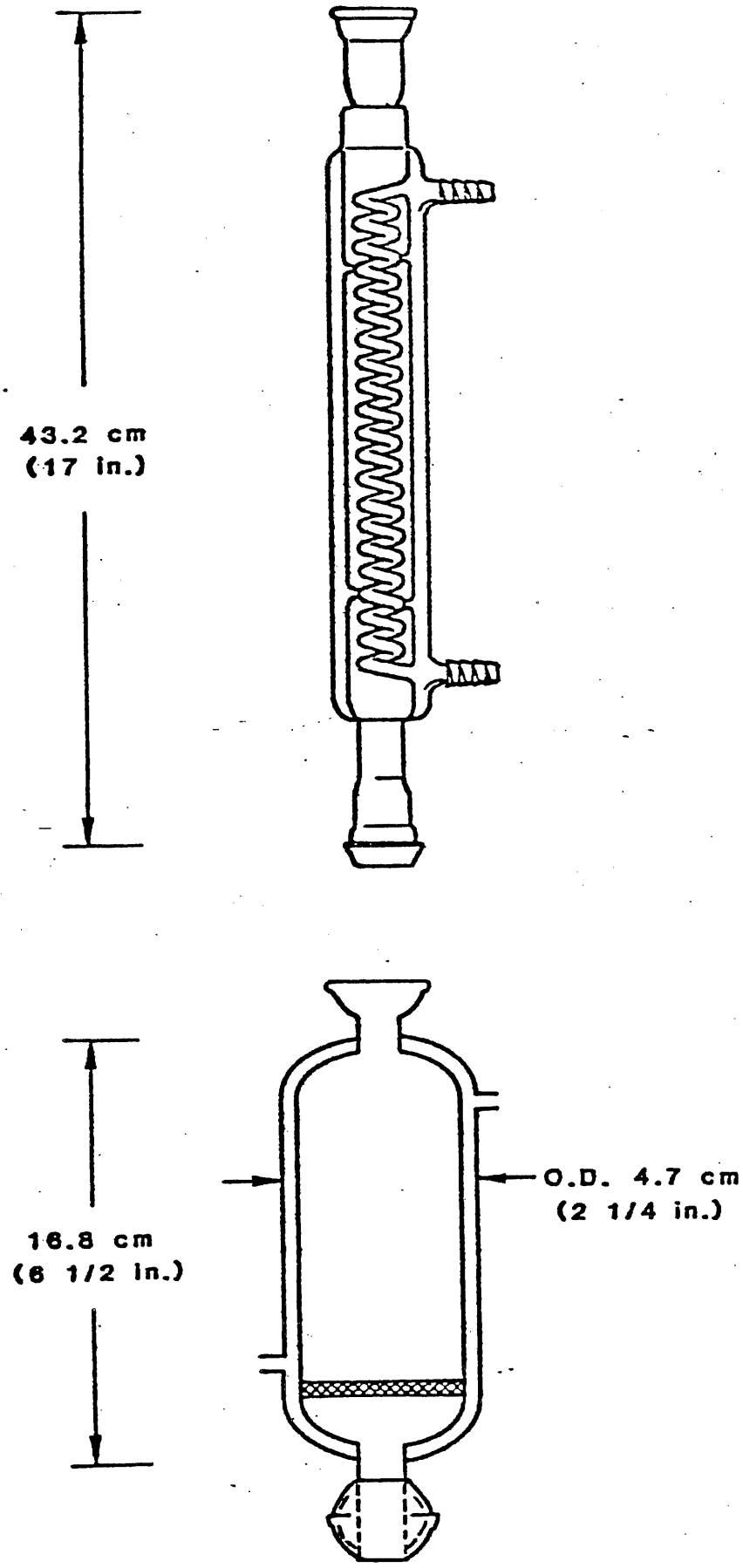

Fig. 2 Acceptable Sorbent Module Design #1

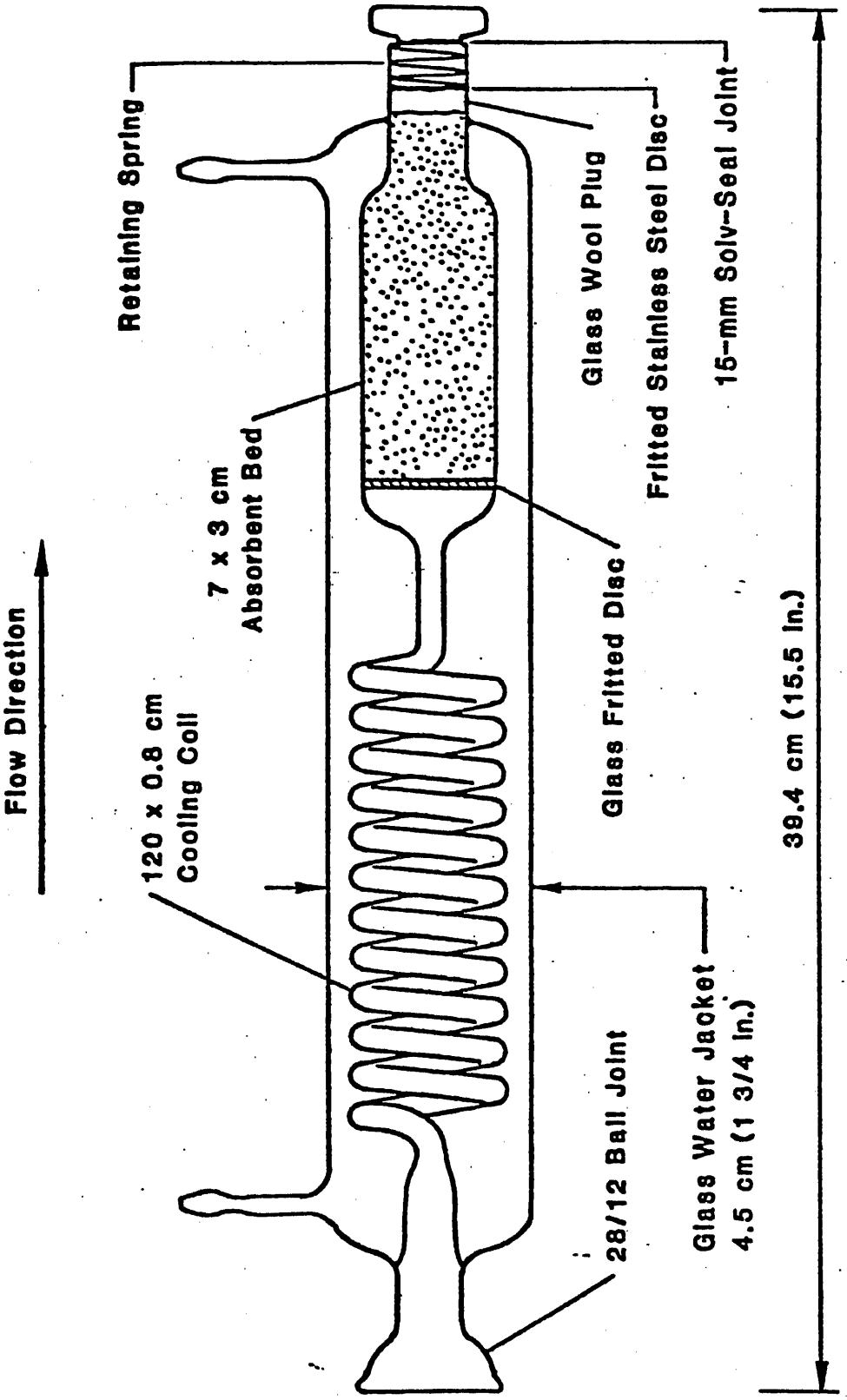

Fig. 3 Acceptable Sorbent Module Design #2

7.2 Sample Recovery, Supplies, and Equipment

7.2.1 Ground Glass Caps or Hexane Rinsed Aluminum Foil

To cap off adsorbent tube and the other sample-exposed portions of the train. If TFE® screw connections are used, then TFE® screw caps shall be used.

7.2.2 Teflon FEP® Wash Bottle

Three 500 ml, Nalgene No. 0023A59, or equivalent.

7.2.3 Probe and Transfer Line Brush

Inert bristle brush with stainless steel rod-handle of sufficient length that is compatible with the liner or probe and transfer line.

7.2.4 Filter Storage Containers

Sealed filter holder or precleaned, wide-mouth amber glass containers with TFE®-lined screw caps or wrapped in hexane rinsed aluminum foil.

7.2.5 Balance

Triple beam, Ohaus model 7505, or equivalent.

7.2.6 Aluminum Foil

Heavy duty, hexane-rinsed.

7.2.7 Precleaned Metal Can

To recover used silica gel.

7.2.8 Precleaned Graduated Cylinder, e.g., 250 ml

250 ml, with 2 ml graduations, borosilicate glass.

7.2.9 Liquid Sample Storage Containers

Precleaned amber glass bottles or clear glass bottles wrapped in opaque material, 1 L, with TFE®-lined screw caps.

8. REAGENTS

8.1 Sampling

8.1.1 Filter -- Fiberglass Reeve-Angel 934 AH or Equivalent

Prior to use in the field, each lot of filters shall be subjected to precleaning and a quality control (QC) contamination check to confirm that there are no contaminants present that will

interfere with the analysis of analyte at the target detection limits.

If performed, filter precleaning shall consist of Soxhlet extraction, in batches not to exceed 50 filters, with the solvent(s) to be applied to the field samples. As a QC check, the extracting solvent(s) shall be subjected to the same concentration, cleanup and analysis procedures to be used for the field samples. The background or blank value observed shall be converted to a per filter basis and shall be corrected for any differences in concentration factor between the QC check (CF_{QC}) and the actual sample analysis procedure (CF_s).

$$\text{Blank value per filter} = \frac{\text{Apparent } \mu g \text{ of analyte}}{\text{No. filters extracted}} \times \frac{CF_s}{CF_{QC}}$$

where:

$$CF = \frac{\text{Initial volume of extracting solvent}}{\text{Final Volume of concentrated extract}}$$

The quantitative criterion for acceptable filter quality will depend on the detection limit criteria established for the field sampling and analysis program. Filters that give a background or blank signal per filter greater than or equal to the target detection limit for the analyte(s) of concern shall be rejected for field use. Note that acceptance criteria for filter cleanliness depends not only on the inherent detection limit of the analysis method but also on the expected field sample volume and on the desired limit of detection in the sampled stream.

If the filters do not pass the QC check, they shall be re-extracted and the solvent extracts re-analyzed until an acceptably low background level is achieved.

8.1.2 Amberlite XAD-2 Resin

The cleanup procedure may be carried out in a giant Soxhlet extractor, which will contain enough Amberlite XAD-2® resin (XAD-2) for several sampling traps. An all glass thimble 55-90 mm OD x 150 mm deep (top to frit) containing an extra coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The XAD-2 must be carefully retained in the extractor cup with a glass wool plug and stainless steel screen since it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse with 1 L H_2O for 1 cycle, then discard H_2O

Water	Extract with H_2O for 8 hr
Methyl alcohol	Extract for 22 hr
Methylene chloride	Extract for 22 hr
Hexane	Extract for 22 hr

The XAD-2 must be dried by one of the following techniques.

(a) After evaluation of several methods of removing residual solvent, a fluidized-bed technique has proven to be the fastest and most reliable drying method.

A simple column with suitable retainers as shown in Fig. 4 will serve as a satisfactory column. A 10.2 cm (4 in.) diameter Pyrex pipe 0.6 m (2 ft. long) will hold all of the XAD-2 from the Soxhlet extractor, with sufficient space for fluidizing the bed while generating a minimum XAD-2 load at the exit of the column.

The gas used to remove the solvent is the key to preserving the cleanliness of the XAD-2. Liquid nitrogen from a regular commercial liquid nitrogen cylinder has routinely proven to be a reliable source of large volumes of gas free from organic contaminants. The liquid nitrogen cylinder is connected to the column by a length of precleaned 0.95 cm (3/8 in.) copper tubing, coiled to pass through a heat source. As nitrogen is bled from the cylinder, it is vaporized in the heat source and passes through the column. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40°C. Experience has shown that about 500 g of XAD-2 may be dried overnight consuming a full 160 L cylinder of liquid nitrogen.

As a second choice, high purity tank nitrogen may be used to dry the XAD-2. The high purity nitrogen must first be passed through a bed of activated charcoal approximately 150 mL in volume. With either type of drying method, the rate of flow should gently agitate the bed. Excessive fluidation may cause the particles to break up.

(b) As an alternate, if the nitrogen process is not available, the XAD-2 may be dried in a vacuum oven, if the temperature never exceeds 20°C.

The XAD-2, even if purchased clean, must be checked for both methylene chloride and hexane residues, plus normal blanks before use.

(c) Storage of Clean XAD-2: XAD-2 cleaned and dried as prescribed above is suitable for immediate use in the field, provided it passes the QC contamination check described in (d), below. However, precleaned dry XAD-2 may develop unacceptable levels of contamination if stored for periods exceeding a few weeks.

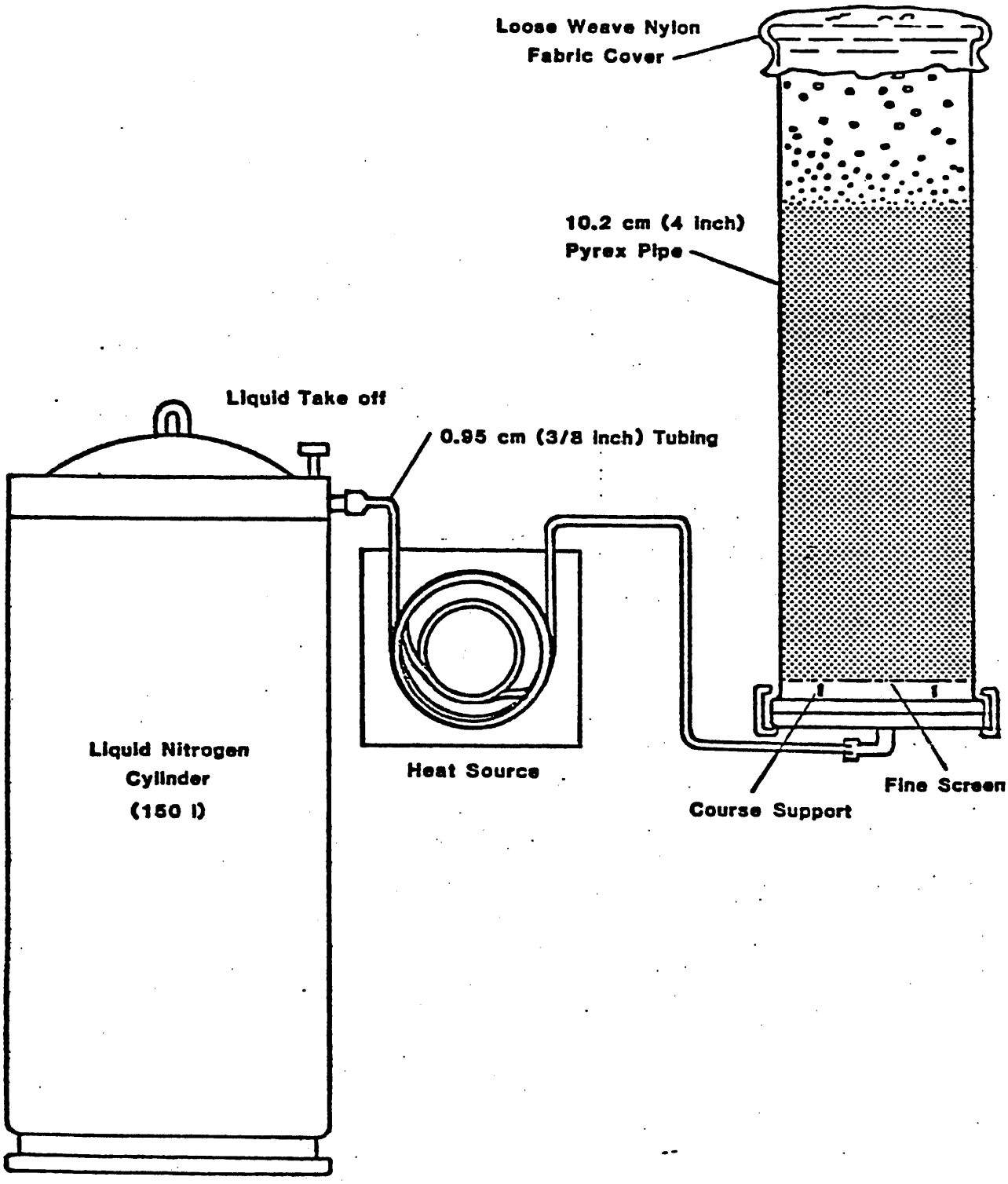

Fig. 4 XAD-2 Fluidized-Bed Drying Apparatus

If precleaned XAD-2 is not to be used immediately, it shall be stored under distilled-in-glass methanol. No more than two weeks prior to initiation of field sampling, the excess methanol shall be decanted; the XAD-2 shall be washed with a small volume of methylene chloride and dried with clean nitrogen as described in (b) above. An aliquot shall then be taken for the QC contamination check described in (d), below.

If the stored XAD-2 fails the QC check, it may be recleaned by repeating the final two steps of the extraction sequence above: sequential methylene chloride and hexane extraction. The QC contamination check shall be repeated after the XAD-2 is recleaned and dried.

(d) QC Contamination Check: The XAD-2, whether purchased, "precleaned", or cleaned as described above, shall be subjected to a QC check to confirm the absence of any contaminants that might cause interferences in the subsequent analysis of field samples. An aliquot of XAD-2, equivalent in size to one field sampling tube charge, shall be taken to characterize a single batch of XAD-2.

The XAD-2 aliquot shall be subjected to the same extraction, concentration, cleanup, and analytical procedure(s) as is (are) to be applied to the field samples. The quantitative criteria for acceptable XAD-2 quality will depend on the detection limit criteria established for the field sampling and analysis program. XAD-2 which yields a background or blank signal greater than or equal to that corresponding to one-half the MDL for the analyte(s) of concern shall be rejected for field use. Note that the acceptance limit for XAD-2 cleanliness depends not only on the inherent detection limit of the analytical method but also on the expected field sample volume and on the desired limit of detection in the sampled stream.

8.1.3 Glass Wool

Cleaned by thorough rinsing, i.e., sequential immersion in three aliquots of hexane, dried in a 110°C oven, and stored in a hexane-washed glass jar with TFE®-lined screw cap.

8.1.4 Water

Deionized, then glass-distilled, and stored in hexane-rinsed glass containers with TFE®-lined screw caps.

8.1.5 Silica Gel

Indicating type, 6-16 mesh. If previously used, dry at 175±5C for 2 hr. New silica gel may be used as received.

8.1.6 Crushed Ice

Place crushed ice in the water bath around the impingers during sampling.

DRAFT

9. SAMPLE RECOVERY REAGENTS

9.1 Acetone

Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers. A blank must be screened by the analytical detection method.

9.2 Hexane

Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers. A blank must be screened by the analytical detection method.

10. PROCEDURE

Caution: Sections 10.1.1.2 and 10.1.1.3 shall be done in the laboratory.

10.1 Sampling

10.1.1 Pretest Preparation

All train components shall be maintained and calibrated according to the procedure described in APTD-0576 unless otherwise specified herein.

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a precleaned glass container or wrapped hexane-rinsed aluminum foil.

10.1.1.1 Preliminary Determinations

Select the sampling site and the minimum number of sampling points according to EPA Method 1. Determine the stack pressure, temperature, and the range of velocity heads using EPA Method 2; it is recommended that a leak-check of the pitot lines (see EPA Method 2, Sec. 3.1) be performed. Determine the moisture content using EPA Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate-settings. Determine the stack gas dry molecular weight, as described in EPA Method 2, Sec. 3.6; if integrated EPA Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the EPA Method 4 sampling.

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of EPA Method 2).

Select a suitable probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 min., and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume determined in Section 6.3. The latter is based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid time-keeping errors.

10.1.1.2 Cleaning Glassware

All glass parts of the train upstream of and including the sorbent module and the first impinger should be cleaned as described in Section 3A of the 1980 issue of "Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples."[3] Special care should be devoted to the removal of resi dual silicone grease sealants on ground glass connections of used glassware. These grease residues should be removed by soaking several hours in a chromic acid cleaning solution prior to routine cleaning as described above.

10.1.1.3 Amberlite XAD-2 Resin Trap

Use a sufficient amount (at least 30 gms or 5 gms/m^3 of stack gas to be sampled) of cleaned XAD-2 to fill completely the glass sorbent trap which has been thoroughly cleaned as prescribed and rinsed with hexane. Follow the XAD-2 with hexane-rinsed glass wool and cap both ends. These caps should not be removed until the trap is fitted into the train. See Fig. 1 for details.

The dimensions and XAD-2 capacity of the sorbent trap, and the volume of gas to be sampled, should be varied as necessary to ensure efficient collection of the species of interest. Some illustrative data are presented in Table 1.

10.1.2 Preparation of Collection Train

During preparation and assembly of the sampling train, keep all train openings where contamination can enter covered until

TABLE 1

SAMPLE SIZE AND FLOW RATE COMPARISON FOR SEVERAL SORBENT TRAP DESIGNS

Trap	Dimensions (mm)		Charge of XAD-2 Resin (g)	Flow Equivalent to 43 cm/sec [a]	Max. Sample Size (cm^3) for Efficient Capture of Following Compounds[b]		
	Depth	Diameter			Octane	Benzene	Phenol
SASS	70	90	130	165 Lpm (5.9 cfm)	150	3.0	240
ADL	70	45	40	40 Lpm (1.5 cfm)	45	0.9	74
Battelle	70	30	19	18 Lpm (0.65 cfm)	22	0.4	35

[a] Upper limit beyond which collection efficiency drops off.

[b] Calculated from Vg^T for 50% breakthrough. Specified value includes a safety factor of 2.

just prior to assembly or until sampling is about to begin. Caution: Do not use sealant greases in assembling the train.

Place approximately 100 gms of water in each of the first two impingers with a graduated cylinder, and leave the third impinger empty. Place approximately 200 to 300 g or more, if necessary, of silica gel in the last impinger. Weigh each impinger (stem included) and record the weights on the impingers and on the data sheet.

Assemble the train as shown in Fig. 1.

Place crushed ice in the water bath around the impingers.

10.1.3 Leak Check Procedures

10.1.3.1 Initial Leak Check

The train, including the probe, will be leak checked prior to being inserted into the stack after the sampling train has been assembled. Turn on and set (if applicable) the heating/cooling system(s) to cool the sample gas yet remain at a temperature sufficient to avoid condensation in the probe and connecting line to the first impinger (approximately 120°C). Allow time for the temperature to stabilize. Leak check the train at the sampling site by plugging the nozzle with a TFE® plug and pulling a 380 mm Hg (12 in. Hg) vacuum. A leakage rate in excees of 4% of the average sampling rate or 0.0057 m^3/min (0.02 cfm) whichever is less, is unacceptable. Sampling must cease if pressure during sampling exceeds the leak check pressure.

The following leak check instruction for the sampling train described in APTD-0576[2] and APTD-0581[4] may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until 380 mm Hg (12 in. Hg) vacuum is reached. Do not reverse the direction of the bypass valve. This will cause water to back up into the probe. If 380 mm Hg (12 in. Hg) is exceeded during the test, either leak check at this higher vacuum or end the leak check as described below and start the test over.

When the leak check is completed, first slowly remove the TFE® plug from the inlet to the probe then immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the probe.

10.1.3.2 Leak Checks During a Test

A leak check shall be performed before and after a change of port during a test. A leak check shall be performed before and after a component (e.g., filter or optional water knockout trap) is changed during a test.

Such leak checks shall be performed according to the procedure given in Section 10.1.3.1 of this method except that it shall be performed at a vacuum equal to or greater than the highest value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate (whichever is smaller) the results are acceptable. If, however, a higher leakage rate is observed, the tester shall either: (1) record the leakage rate and then correct the volume of gas sampled since the last leak check as shown in Section 10.1.3.4 of this method, or (2) void the test.

10.1.3.3 Post-Test Leak Check

A leak check is mandatory at the end of a test. This leak check shall be performed in accordance with the procedure given in Section 10.1.3.1 except that it shall be conducted at a vacuum equal to or greater than the highest value recorded during the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate (whichever is smaller), the results are acceptable. If, however, a higher leakage rate is observed, the tester shall either: (1) record the leakage rate and correct the volume as gas sampled since the last leak check as shown in Section 10.1.3.4 of this method, or (2) void the test.

10.1.3.4 Correcting for Excessive Leakage Rates

The equation given in Section 11.3 of this method for calculating $V_m(std)$, the corrected volume of gas sampled, can be used as written unless the leakage rate observed during any leak check after the start of a test exceeded L_a, the maximum acceptable leakage rate (see definitions below). If an observed leakage rate exceeds L_a, then replace V_m in the equation in Section 11.3 with the following expression:

$$\left[V_m - \sum_{i=1}^{n} (L_i - L_a)\,\theta_i - (L_p - L_a)\,\theta_p\right]$$

where:

V_m = Volume of gas sampled as measured by the dry gas meter (dscf).

L_a = Maximum acceptable leakage rate equal to 0.00057 m^3/min. (0.02 ft^3/min) or 4% of the average sampling rate, whichever is smaller.

L_p = Leakage rate observed during the post-test leak check, m^3/min (ft^3/min).

L_i = Leakage rate observed during the leak check performed prior to the "i th" leak check (i = 1,2,3...n), m^3/min (ft^3/min).

θ_i = Sampling time interval between two successive leak checks beginning with the interval between the first and second leak checks, min.

θ_p = Sampling time interval between the last (n th) leak check and the end of the test, min.

Substitute only for those leakages (L_i or L_p) which exceeded L_a.

10.1.3.5 Train Operation

During the sampling run, a sampling rate within 10% of the selected sampling rate shall be maintained. Data will be considered acceptable if readings are recorded at least every 5 min. and not more than 10% of the point readings are in excess of ±10% and the average of the point readings is within ±10%. During the run, if it becomes necessary to change any system component in any part of the train, a leak check must be performed prior to restarting.

For each run, record the data required on the data sheets. An example is shown in Fig. 4. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment and when sampling is halted.

To begin sampling, remove the nozzle cap, verify (if applicable) that the probe and sorbent module temperature control systems are working and at temperature and that the probe is properly positioned. Position the probe at the sampling point. Immediately start the pump and adjust the flow rate.

If the stack is under significant sub-ambient pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to avoid water backing into the probe. If necessary, the pump may be turned on with the coarse adjust valve closed.

During the test run, make periodic adjustments to keep the probe temperature at the proper value. Add more ice and, if necessary, salt to the ice bath. Also, periodically check the level and zero of the manometer and maintain the temperature of sorbent module at or less than 20°C but above 0°C.

If the pressure drop across the train becomes high enough to make the sampling rate difficult to maintain, the test run shall be terminated unless the replacing of the filter corrects the problem. If the filter is replaced, a leak check shall be performed.

At the end of the sample run, turn off the pump, remove the probe and nozzle from the stack, and record the final dry gas meter reading. Perform the post test leak check.*

*With acceptability of the test run to be based on the same criterion as in 10.1.3.1.

FIEL[illegible]

PLANT _____
DATE _____
SAMPLING LOCATION _____
SAMPLE TYPE _____
RUN NUMBER _____
OPERATOR _____
BAROMETRIC PRESSURE _____
SITE TO BARO. ELEVATION (ft.) _____
CORRECTED B.P. _____
STATIC PRESSURE (P_s) _____
FILTER NUMBER(s) _____

LEAK CHECK: Initial at ≥ 15" Hg CFM _____
Final at _____ "Hg CFM _____
Pitot at ≥3" H_2O _____

PROBE LENGTH AND TYPE _____
NOZZLE I.D. _____
ASSUMED MOISTURE, % _____
SAMPLE BOX NUMBER _____
METER BOX NUMBER _____
TEMPERATURE METER NO _____
THERMOCOUPLE I.D. NO _____
METER ΔH _____
METER CORRECTION _____
C FACTOR _____
REFERENCE Δp _____
UMBILICAL CORD I.D. NO _____

SCHEMATIC OF TRAVERSE POINT LAYOUT
Read and Record All Data
Every _____ Minutes

$$Vm_I = \_\_\_\_\_ (Tm + 460)\sqrt{\frac{\Delta Ps}{Ts + 460}}$$

TRAVERSE POINT NUMBER	CLOCK TIME (24 hr CLOCK) / SAMPLING TIME, min	GAS METER READING (V_m), ft^3		VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
		DESIRED	ACTUAL		DESIRED	~~ACTUAL~~		INLET ($T_{m_{in}}$), °F	OUTLET ($T_{m_{out}}$), °F		XAD-2	
										3		2

Dis from Port

Comments

10.2 Sample Recovery

Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period.

When the probe can be safety handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with hexane-rinsed aluminum foil. Seal off the inlet to the train with a ground glass cap or hexane-rinsed aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area should be clean and enclosed so that the chances of contaminating or losing the sample will be minimized. No smoking shall be allowed.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, color of the impinger liquid, etc. Treat the samples as follows:

10.2.1 Container No. 1

Either seal the ends of the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of precleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and/or a sharp-edged blade. Seal the container.

10.2.2 Sorbent Modules

Remove the sorbent module from the train and cap it off.

10.2.3 Cyclone Catch

If the optional cyclone is used, quantitatively recover the particulate into a sample container and cap.

10.2.4 Sample Container No. 2

Quantitatively recover material deposited in the nozzle, probe, transfer line, the front half of the filter holder, and the cyclone, if used, first by brushing and then by sequentially rinsing with acetone and then hexane three times each and add all these rinses to Container No. 2. Mark level of liquid on container.

10.2.5 Sample Container No. 3

Rinse the back half of the filter holder, the connecting line between the filter and the condenser and the condenser (if using the separate condenser-sorbent trap) three times each with acetone

and hexane collecting all rinses in Container 3. If using the combined condenser-sorbent trap, the rinse of the condenser shall be performed in the laboratory after removal of the XAD-2. If the optional water knockout trap has been employed, it shall be weighed and recorded and its contents placed in Container 3 along with the rinses of it. Rinse it three times each with acetone, and hexane. Mark level of liquid on container.

10.2.6 Sample Container No. 4

Remove the first impinger. Wipe off the outside of the impinger to remove excessive water and other material, weigh (stem included), and record the weight on data sheet. Pour the contents and rinses directly into Container No. 4. Rinse the impinger sequentially three times with acetone, and hexane. Mark level of liquid on container.

10.2.7 Sample Container No. 5

Remove the second and third impingers, wipe the outside to remove excessive water and other debris, weigh (stem included) and record weight on data sheet. Empty the contents and rinses into Container No. 5. Rinse each with distilled DI water three times. Mark level of liquid on container.

10.2.8 Silica Gel Container

Remove the last impinger, wipe the outside to remove excessive water and other debris, weigh (stem included), and record weight on data sheet. Place the silica gel into its marked container.

11. CALCULATIONS

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

11.1 Nomenclature

G_s = Total weight of chlorinated organic compounds in stack gas sample, ng.

C_s = Concentration of chlorinated organic compounds in stack gas, $\mu g/m^3$, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

I = Percent of isokinetic sampling.

M_w = Molecular weight of water, 18 g/g-mole (18 lb/lb-mole)

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-$m^3/{}^oK$-g-mole (21.83 in. Hg-$ft^3/{}^oR$-lb-mole).

T_m = Absolute average dry gas meter temperature ^oK (^oR).

T_s = Absolute average stack gas temperature ^oK (^oR).

T_{std} = Standard absolute temperature, 293^oK (68^oF).

m_{lc} = Total mass of liquid collected in impingers and silica gel.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_m(std)$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).

$V_w(std)$ = Volume of water vapor in the gas sample corrected to standard conditions, scm (scf).

v_s = Stack gas velocity, calculated by combustion calculation, m/sec (ft/sec).

Y = Meter box correction factor.

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

11.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop

See data sheet (Fig. 5).

11.3 Dry Gas Volume

Correct the sample volume measured by the dry gas meter to standard conditions [20°C, 760 mm Hg (68±F, 29.92 in. HG)] by using Equation 1.

$$V_m(std) = Y\, V_m \frac{T_{std}}{T_m} \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} = K_1 V_m \frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m} \quad (1)$$

where:

K_1 = 0.3855 °K/mm Hg for metric units

= 17.65 °R/in. Hg for English units

11.4 Volume of Water Vapor

$$V_w(std) = m_{lc} \frac{RT_{std}}{M_w \times P_{std}} = K_2 m_{lc} \quad (2)$$

where:

K_2 = 0.00134 m^3/ml for metric units

= 0.0472 ft^3/ml for English units

11.5 Moisture Content

$$B_{ws} = \frac{V_w(std)}{V_m(std) + V_w(std} \quad (3)$$

If liquid droplets are present in the gas stream assume the stream to be saturated and use a psychrometric chart to obtain an approximation of the moisture percentage.

11.6 Percent Isokinetic Sampling

$$I = \frac{100\, T_s\, [K_4\, m_{lc} + (V_m\, K_m)\, (P_{bar} + \Delta H/13.6]}{60\, \theta_{vs}\, P_s\, A_n} \quad (4)$$

where:

K_4 = 0.003454 mm Hg - m^3/ml - °K for metric units

= 0.002669 in Hg - ft^3/ml - °R for English units

11.7 Concentration of Chlorinated Organic Compounds in Stack Gas

Determine the concentration of chlorinated organic compounds in the stack gas according to Equation 5.

$$C_s = K_5 \frac{G_s}{V_m(std)} \qquad (5)$$

where:

$$K_5 = 35.31 \text{ ft}^3/\text{m}^3$$

12. QUALITY ASSURANCE (QA) PROCEDURES

The positive identification and quantification of specific compounds in this assessment of stationary conventional combustion sources is highly dependent on the integrity of the samples received and the precision and accuracy of all analytical procedures employed. The QA procedures described in this section were designed to monitor the performance of the sampling methods and to provide information to take corrective actions if problems are observed.

Field Blanks

The field blanks should be submitted as part of the samples collected at each particular testing site. These blanks should consist of materials that are used for sample collection and storage and are expected to be handled with exactly the same procedure as each sample medium.

Blank Train

For each series of test runs, set up a blank train in a manner identical to that described above, but with the probe inlet capped with hexane-rinsed aluminum foil and the exit end of the last impinger capped with a ground glass cap. Allow the train to remain assembled for a period equivalent to one test run. Recover the blank sample as described in Sec. 7.2.

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DRAFT

ANALYTICAL PROCEDURES TO ASSAY STACK EFFLUENT SAMPLES AND RESIDUAL COMBUSTION PRODUCTS FOR POLYCHLORINATED DIBENZO-p-DIOXINS (PCDD) AND POLYCHLORINATED DIBENZOFURANS (PCDF)

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DRAFT

1. Scope and Applicability of Method

The analytical procedures described here are applicable for the determination of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in stack effluents from combustion processes. These methods are also applicable to residual combustion products such as bottom and precipitator ash. The methods presented entail addition of isotopically-labeled internal standards to all samples in known quantities, extraction of the sample with appropriate organic solvents, preliminary fractionation and cleanup of the extracts using a sequence of liquid chromatography columns, and analysis of the processed extract for PCDD and PCDF using coupled gas chromatography - mass spectrometry (GC-MS). Various performance criteria are specified herein which the analytical data must satisfy for quality assurance purposes. These represent minimum criteria which must be incorporated into any program in which PCDD and PCDF are determined in combustion product samples.

The method presented here does not yield definitive information on the concentration of individual PCDD/PCDF isomers, except for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) and 2,3,7,8-Tetrachlorodibenzofuran (TCDF). Rather, it is designed to indicate the total concentration of the isomers of several chlorinated classes of PCDD/PCDF (that is, total tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins and dibenzofurans). Of the 75 separate PCDD and 135 PCDF isomers, there are 22 TCDD, 38 TCDF, 14 PeCDD, 28 PeCDF, 10 HxCDD, 16 HxCDF, 2 HpCDD, 4 HpCDF, 1 OCDD and 1 OCDF.[a]

The analytical method presented herein is intended to be applicable for determining PCDD/PCDF present in combustion products at the ppt to ppm level, but the sensitivity which can ultimately be achieved for a given sample will depend upon the types and concentrations of other chemical compounds in the sample.

The method described here must be implemented by or under the supervision of chemists with experience in handling supertoxic materials and analyses should only be performed in rigorously controlled, limited access laboratories. The quantitation of PCDD/PCDF should be accomplished only by analysts experienced in utilizing capillary-column gas chromatography-mass spectrometry to accomplish quantitation of chlorocarbons and similar compounds at very low concentration.

The toxicological data which are available for the PCDD and PCDF are far from complete. That is, the toxicological properties of all of the isomers comprising the 75 possible PCDD and 135 possible PCDF are not presently known. However, a considerable body of toxicological data exists for 2,3,7,8-TCDD which indicates that, in certain animal species, this compound is lethal at extraordinarily low does and causes a wide range of systemic affects, including hepatic disorders, carcinoma and birth defects. While much less data is available regarding the toxicology of 2,3,7,8-TCDF, sufficient data is available to form the basis for the belief that 2,3,7,8-TCDF is similar in its toxicological properties to 2,3,7,8-TCDD. Relatively little is known about the toxicology of the higher chlorinated PCDD and PCDF (that is, penta through octachlorinated PCDD/PCDF), although there is some data to suggest that certain penta-, hexa-, and hepta- PCDD/PCDF isomers are hazardous. In view of the extraordinary toxicity of 2,3,7,8-TCDD and in view of the exceptional biological activity of this compound (on the basis of enzyme induction assays) and of compounds having similar molecular structures, extensive precautions are required to preclude exposure to personnel during handling and analysis of materials containing these compounds and to prevent contamination of the laboratory. Specific safety and handling procedures which are recommended are given in the Appendix to this protocol.

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a. The abbreviations which are used to designate chlorinated dibenzo-p-dioxins and dibenzofurans throughout this document are as follows:

PCDD - Any or all of the 75 possible chlorinated dibenzo-p-dioxin isomers

PCDF - Any or all of the 135 possible chlorinated dibenzofuran isomers

TCDD - Any or all of the 22 possible tetrachlorinated dibenzo-p-dioxin isomers

TCDF - Any or all of the 138 possible tetrachlorinated dibenzofuran isomers

PeCDD - Any or all of the 14 possible pentachlorinated dibenzo-p-dioxin isomers

PeCDF - Any or all of the 28 possible pentachlorinated dibenzofuran isomers

HxCDD - Any or all of the 10 possible hexachlorinated dibenzo-p-dioxin isomers

HXCDF - Any or all of the 16 possible hexachlorinated dibensofuran isomers

HpCDD - Any or all of the 2 possible heptachlorinated dibenzo-p-dioxin isomers

HpCDF - Any or all of the 4 possible heptachlorinated dibenzofuran isomers

OCDD - Octachlorodibenzo-p-dioxin

OCDF - Octachlorodibenzofuran

Specific Isomers. - Any of the abbreviations cited above may be converted to designate a specific isomer by indicating the exact positions (carbon atoms) where chlorines are located within the molecule. For example, 2,3,7,8-TCDD refers to only one of the 22 possible TCDD isomers - that isomer which is chlorinated in the 2,3,7,8 positions of the dibenzo-p-dioxin ring structure.

2. Reagents and Chemicals

The following reagents and chemicals are appropriate for use in these procedures. In all cases, equivalent materials from other suppliers may also be used.

2.1 Potassium Hydroxide, Anhydrous, Granular Sodium Sulfate and Sulfuric Acid (all Reagent Grade): J. T. Baker Chemical Co. or Fisher Scientific Co. The granular sodium sulfate is purified prior to use by placing a beaker containing the sodium sulfate in a 400°C oven for four hours, then removing the beaker and allowing it to cool in a desiccator. Store the purified sodium sulfate in a bottle equipped with a Teflon-lined screw cap.

2.2 Hexane, Methylene Chloride, Benzene, Methanol, Toluene, Isooctane: "Distilled in Glass" Burdick and Jackson.

2.3 Tridecane (Reagent Grade): Sigma Chemical Co.

2.4 Basic Alumina (Activity Grade 1, 100 - 200 mesh): ICN Pharmaceuticals. Immediately prior to use, the alumina is activated by heating for at least 16 hours at 600°C in a muffle furnace and then allowed to cool in a desiccator for at least 30 minutes prior to use. Store pre-conditioned alumina in a desiccator.

2.5 Silica (Bio-Sil A, 100/200 mesh): Bio-Rad. The following procedure is recommended for conditioning the Bio-Sil A prior to use. Place an appropriate quantity of Bio-Sil A in a 30 mm x 300 mm long glass tube (the silica gel is held in place by glass wool plugs) which is placed in a tube furnace. The glass tube is connected to a pre-purified nitrogen cylinder, through a series of four traps (stainless steel tubes, 1.0 cm O.D. x 10 cm long)[6]: 1) Trap No. 1 - Mixture comprised of Chromosorb W/AW (60/80 mesh coated with 5% Apiezon L), Graphite (UCP-1-100), Activated Carbon (50 to 200 mesh) in a 7:1.5:1.5 ratio (Chromosorb W/AW, Apiezon L obtained from Supelco, Inc., Graphite obtained from Ultracarbon Corporation, 100 mesh, 1-M-USP; Activated Carbon obtained from Fisher Scientific Co.); 2) Trap No. 2 - Molecular Sieve 13 X (60/80 mesh), Supelco, Inc.; 3) Trap No. 3 - Carbosieve S (80/100 mesh), obtained from Supelco, Inc.; 4) The Bio-Sil A is heated in the tube for 30 minutes at 180°C while purging with nitrogen (flow rate 50-100 mL/minute), and the tube is then removed from the furnace and allowed to cool to room temperature. Methanol (175 mL) is then passed through the tube, followed by 175 mL methylene chloride. The tube containing the silica is then returned to the furnace, the nitrogen purge is again established (50-100 mL flow) and the tube is heated at 50°C for 10 minutes, then the temperature is gradually increased to 180°C over 25 minutes and maintained at 180°C for 90 minutes. Heating is then discontinued but the nitrogen purge is continued until the tube

cools to room temperature. Finally, the silica is transferred to a clean, dry, glass bottle and capped with a Teflon-lined screw cap for storage.

2.6 Silica Gel Impregnated With Sulfuric Acid: Concentrated sulfuric acid (44 g) is combined with 100 g Bio-Sil A (conditioned as described above) in a screw capped bottle and agitated to mix thoroughly. Aggregates are dispersed with a stirring rod until a uniform mixture is obtained. The H_2SO_4-silica gel is stored in a screw-capped bottle (Teflon-lined cap).

2.7 Silica Gel Impregnated with Sodium Hydroxide: 1N Sodium hydroxide (39 g) is combined with 100 g Bio-Sil A (conditioned as described above) in a screw capped bottle and agitated to mix throughly. Aggregates are dispersed with a stirring rod until a uniform mixture is obtained. The NaOH-silica gel is stored in a screw-capped bottle (Teflon-lined cap).

2.8 Carbon/Celite:
Carbon: Amoco PX-21
Celite 545: Fisher Scientific Co

Combine Amoco PX-21 carbon (10.7 g) with Celite 545 (124 g) in a 250 mL glass bottle fitted with a Teflon-lined cap. Agitate the mixture to combine thoroughly. Store in the screw-capped bottle.

2.9 Sepralyte Diol (40μ): Analytichem International

2.10 Nitrogen and Hydrogen (Ultra High Purity): Matheson Scientific

3. Apparatus and Materials

The following apparatus and materials are appropriate for use in these procedures. In all cases, equivalent items from other suppliers may also be used.

3.1 Glassware used in the analytical procedures (including the Soxhlet apparatus and disposable bottles) is cleaned by rinsing successively three times with methanol and then three times with methylene chloride, and finally drying it in a 100°C oven. Bottles cleaned in this manner are allowed to cool to room temperature and are then capped using Teflon-lined lids. Teflon cap liners are rinsed as just described but are allowed to air-dry. More rigorous cleaning of some glassware with detergent may be required prior to the solvent rinses, for example, the glassware employed for Soxhlet extraction of samples.

3.1.1 Sample Vessels: 125 mL and 250 mL flint glass bottles fitted with screw caps and teflon cap liners, and glass test tubes, VWR-Scientific.

3.1.2 Teflon Cap Liners: Scientific Specialities Service, Inc.

3.1.3 Soxhlet Apparatus: Extraction apparatus, Allihn condenser, Kimax Brand, American Scientific Products Cat. No. E6252-2A.

3.1.4 Gravity Flow Liquid Chromatographic Columns: Custom Fabricated (Details of the columns are provided in later sections).

3.1.5 Micro-vials (3.0 mL): Reliance Glass.

3.2 Capillary Gas Chromatographic Columns: Two different columns are required if data on both 2,3,7,8-TCDD and 2,3,7,8-TCDF, as well as on the total PCDD/PCDF by chlorinated class, are desired. The appropriate columns are: 1) A fused silica column (60 M x 0.25 mm I.D.) coated with DB-5 (0.25 μ film thickness), J & S Scientific, Inc., Crystal Lake, IL is utilized to separate each of the several tetra-through octachlorinated CDDs and CDFs, as a group, from all of the other groups. While this column does not resolve all of the isomers within each chlorinated group, it effectively resolves each of the chlorinated groups from all of the other chlorinated groups and therefore provides data on the total concentration of each group (that is, total tetra-, penta-, hexa-, hepta- and octa CDDs and CDFs). This column also resolves 2,3,7,8-TCDD from all of the other 21 TCDD isomers and this isomer can therefore be determined quantitatively if proper calibration procedures are applied as described further in a later section. This column does not completely resolve 2,3,7,8-TCDF from the other TCDF isomers, and if a peak corresponding in retention time to 2,3,7,8-TCDF is observed in the analysis using this column, then a portion of the sample extract must be reanalyzed using the second GC column described below if isomer - specific data on 2,3,7,8-TCDF is desired. 2) A fused silica column (30 M x 0.25 mm I.D.) coated with DB-225 (0.25 μ film thickness), J & S Scientific, Inc., Crystal Lake, IL, must be utilized to obtain quantitative data on the concentration of 2,3,7,8-TCDF, since this column adequately resolves 2,3,7,8-TCDF from the other TCDF isomers.

3.3 Balance: Analytical Balance, readibility, 0.0001 g.

3.4 Nitrogen Blowdown Concentration Apparatus: N-Evap Analytical Evaporator Model III, Organomation Associates Inc.

3.5 Tube Furnace: Lindberg Type 59344.

4. Instrumentation

Gas Chromatograph-Mass Spectrometer-Data System (GC/MS/DS): The instrument system used to analyze sample extracts for PCDD/PCDF comprises a gas chromatograph (fitted for capillary columns) coupled directly or through an enrichment device to a mass spectrometer which is equipped with a computer-based data system. The individual components of the GC/MS/DS are described below.

4.1 Gas Chromatograph (GC): The chromatograph must be equipped with an appropriate injector and pneumatic system to permit use of the specified glass or fused silica capillary columns. It must also incorporate an oven which can be heated in a reproducible, programmed temperature cycle. The injector should be configured for splitless/split injections. The GC column performance should be verified at the beginning of each 8 hour work period or at the beginning of each series of analyses if more than one set of samples is analyzed during an 8 hour shift. Extracts of complex combustion products and effluents may contain numerous organic residues even after application of the extensive prefractionation/cleanup procedures specified in this method. These residues may result in serious deviation of GC column performance and therefore, frequent performance checks are desirable. Using appropriate calibration mixtures, as described below, the retention time windows for each chlorinated class of CDDs/CDFs must be verified. In addition, the GC column utilized must be demonstrated to effectively separate 2,3,7,8-TCDD from all other TCDD isomers if data on 2,3,7,8-TCDD alone is desired with at least 20% valley definition between the 2,3,7,8- isomer and the other adjacent-eluting TCDD isomers. Typically, capillary column peak widths (at half-maximum peak height) on the order of 5-10 seconds are obtained in the course of these analyses. An appropriate GC temperature program for the analyses described herein is discussed in a later section (see Table 1).

4.2 Gas Chromatograph-Mass Spectrometer Interface: The GC-MS interface can include enrichment devices, such as a glass jet separator or a silicone membrane separator, or the gas chromatograph can be directly coupled to the mass spectrometer source, if the system has adequate pumping of the source region. The interface may include a diverter valve for shunting the column effluent and isolating the mass spectrometer source. All components of the interface should be glass or glass-lined stainless steel. The interface components must be compatible with temperatures in the neighborhood of 250°C, which is the temperature at which the interface is typically maintained throughout analyses for PCDD/PCDF. The GC/MS interface must be appropriately configured so that the separation of 2,3,7,8-TCDD from the other TCDD isomers which is achieved in the gas chromatographic column is not appreciably degraded. Cold spots and/or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. If the latter are observed, thorough cleaning of the injection port, interface and connecting lines should be accomplished prior to proceeding.

4.3 Mass Spectrometer (MS): The mass spectrometer used for the analyses described here is typically a double-focusing sector or quadrupole instrument equipped with an electron impact source (70 ev), maintained at 250°C, and a standard electron multiplier detector. If possible, it is desirable to have both low and high resolution capability with the mass spectrometer used, since confirmation of data obtained by low resolution MS using high resolution MS is sometimes desirable. Alternatively, a combination of mass spectrometers can be used for this purpose. The static resolution of the instrument must be maintained at a minimum of 1:500 (with a 10% valley between adjacent masses) if operating in the low resolution MS mode, and a minimum resolution of 1:10,000 is desirable for operation in the high resolution mode. The mass spectrometer must also be configured for rapid computer-controlled selected-ion monitoring in both high and low resolution operating modes. At a minimum, two ion-masses characteristic of each class of chlorinated dioxins should be monitored, and these are two ions in the molecular ion isotopic cluster. It is desirable for increased confidence in the data to also monitor the fragment ions arising from the loss of COCl from the molecular ion. In order to accomplish the requisite rapid multiple ion monitoring sequence during the time period defined by a typically capillary chromatographic peak (the base of the chromatographic peak is typically 15-20 seconds in width), the following MS performance parameters are typically required (assuming a 4-ion monitoring sequence for each class of PCDD/PCDF): dwell time/ion-mass, ≥100 msec.; minimum number of data points/chromatographic peak, 7 . The mass scale of the mass spectrometer is calibrated using high boiling perfluorokerosene and/or some other suitable mass standard depending upon the requirements of the GC-MS-DS system utilized. The actual procedures utilized for calibration of the mass scale will be unique to the particular mass spectrometer being employed. A list of the appropriate ions to be monitored in the PCDD/PCDF analyses described herein is presented in a later section (see Table 1).

4.4 Data System: A dedicated computer-based data system, capable of providing the data described above, is employed to control the rapid selected-ion monitoring sequence and to acquire the data. Both digital data (peak areas or peak heights) as well as peak profiles (displays of intensities of ion-masses monitored as a function of time) should be acquired during the analyses, and displayed by the data system. This raw data (mass chromatograms) should be provided in the report of the data.

5. Calibration Standards

A recommended set of calibration standards to be used in the analyses described herein is presented below. Stock standard solutions of the various PCDD and PCDF isomers and mixtures thereof are prepared in a glovebox, using weighed quantities of the authentic isomers. These stock solutions are contained in appropriate volumetric flasks and are stored tightly stoppered, in a refrigerator. Aliquots of the stock standards are removed for direct use or for subsequent serial dilutions to prepare working standards. These standards must be checked regularly (by comparing instrument response factors for them over a period of

time) to ensure that solvent evaporation or other losses have not occurred which would alter the standard concentration. The several recommended standard solutions are as follows.

5.1 Standard Mixture A: Prepare a stock solution containing the following isotopically-labelled PCDD and PCDF in isooctane at the indicated concentrations: 2.5ng./µl $^{13}C_{12}$-2,3,7,8-TCDD, 2.5ng/µl $^{37}Cl_4$-2,3,7,8-TCDF, 25ng/µL $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, 25ng/µL $^{13}C_{12}$-1,2,3,4,7,8-HxCDF, 25ng/µL $^{13}C_{12}$-OCDD, and 25ng/µL $^{13}C_{12}$-OCDF. Portions of this isomer mixture are added to all samples prior to analyses and serve as internal standards for use in quantitation. Recovery of these standards is also used to guage the overall efficacy of the analytical procedures.

5.2 Standard B: Prepare a stock solution containing 1.0 ng of $^{37}Cl_4$-2,3,7,8-TCDD/µL of isooctane. This standard can be coinjected if desired, along with aliquots of the final sample extract to reliably estimate the recovery of the $^{13}C_{12}$-2,3,7,8-TCDD surrogate standard.

5.3 Standard Mixture C: Prepare a stock solution containing 100 ng/µL of isooctane of each of the following PCDD and PCDF: 2,3,7,8-TCDF; 2,3,7,8-TCDD; 1,3,4,6,8-PeCDF, 2,3,4,6,7-PeCDF; 1,2,4,7.9-PeCDD; 1,2,3,8,9-PeCDD; 1,2,3,4,6,8-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,4,6,8-HxCDD, 1,2,3,4,6,7-HxCDD; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF; 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,9-HpCDD; OCDF: and OCDD. This isomer mixture is used to define the gas chromatographic retention time intervals or windows for each of the penta-, hexa-, hepta-, and octachlorinated groups of PCDD and PCDF. Each pair of isomers of a given chlorinated class which is listed here corresponds to the first and last eluting isomers of that class on the DB-5 capillary GC column (except for TCDD and TCDF). In addition, this isomer mixture is used to determine GC-MS response factors for representative isomers of each of the penta-, hexa-, hepta-, and octachlorinated groups of PCDD and PCDF. The later data are used in quantitating the analytes in unknown samples.

5.4 Standard Mixture D: Prepare a stock solution containing 50 pg/µL of isooctane of each of the following TCDD isomers: 1,3,6,8-TCDD; 1,2,3,7-TCDD; 1,2,3,9-TCDD; 2,3,7,8-TCDD; and 1,2,8,9-TCDD. Two of the isomers in this mixture are used to define the gas chromatographic retention time window for TCDDs (1,3,6,8-TCDD is the first eluting TCDD

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b. Some of the PCDD/PCDF isomer standards recommended for this method are available from Cambridge Isotope Laboratories, Cambridge, Massachusetts. Other PCDD/PCDF standards are available from the Brehm Laboratory, Wright State University, Dayton, Ohio, from the U.S. EPA Standard Repository at Research Triangle Park, North Carolina and possibly from other laboratories. Not all of the indicated isotopically-labelled PCDD/PCDF internal standards recommended here are presently available in quantities sufficient for widespread distribution, but these are expected to be available in the near future.

isomer and 1,2,8,9-TCDD is the last eluting TCDD isomer on the DB-5 GC column). The remaining isomers serve to demonstrate that the 2,3,7,8-TCDD isomer is resolved from the other nearest eluting TCDD isomers, and that the column therefore yields quantitative data for the 2,3,7,8-TCDD isomer alone.

5.5 Standard Mixture E: Prepare a stock solution containing 50 pg/μL of isooctane of each of the following TCDF isomers: 1,3,6,8-TCDF; 2,3,4,8-TCDF; 2,3,7,8-TCDF, 2,3,4,7-TCDF; and 1,2,8,9-TCDF. This isomer mixture is used to define the TCDF gas chromatographic retention time window (1,3,6,8- and 1,2,8,9-TCDF are the first and last eluting TCDFs on the DB-5 capillary column) and to demonstrate that 2,3,7,8-TCDF is uniquely resolved from the adjacent-eluting TCDF isomers.

6. Procedures for Addition of Internal Standards and Extraction of Samples

Both liquid and solid samples will be obtained for PCDD/PCDF analyses as a result of the application of an appropriate stack sampling procedure. Samples resulting from the sampling train will include the following (these will be provided to the analytical laboratory as separate samples in the form indicated): 1) particulate filter and particulates thereon; 2) particulates from the cyclone (if used); 3) combined aqueous solutions from the impingers; 4) the intact XAD-resin cartridge and the resin therein; 5) combined aqueous rinse (if used) solutions from rinses of the nozzle, probe, filter holder, cyclone (if used), impingers, and all connecting lines; 6) combined acetone rinse solutions from rinses of the nozzle, probe, filter holder, cyclone (if used), impingers, and all connecting lines; 7) combined hexane rinse solutions from rinses of the nozzle, probe, filter, cyclone (if used), impingers, and all connecting lines. In addition, samples of bottom ash, precipitator ash, incinerator feed materials or fuel, quench liquids, and materials from effluent control devices may also be provided for analyses.

In general, the volumes of all liquid samples received for analyses are measured and recorded, and where appropriate, solid samples or aliquots thereof are weighed. Any samples which are homogeneous (as for example, a single liquid phase sample or a solid which can be thoroughly mixed) can be split prior to analyses, if desired, provided that this will still permit the attainment of the desired detection limits for the analytes of interest. Samples such as particulates from the sampling train which are generally collected in relatively small quantity, are preferably analyzed in total.

6.1 Organic Liquid Samples (Acetone and Hexane Solutions) Concentrate each of the combined organic liquids (acetone and hexane solutions) to a volume of about 1-5 mL using the nitrogen blowdown

apparatus (a stream of dry nitrogen) while heating the sample gently on a water bath. Pool the concentrated residues, rinsing the vessels three times with small portions of hexane and adding these to the residues, and concentrate to near dryness. This residue will likely contain particulates which were removed in the rinses of the train probe and nozzle. Combine the residue (along with three rinses of the final sample vessel) in the Soxhlet apparatus with the filter and particulates, and proceed as described under Solid Sample below.

6.2 Aqueous Liquids

Add an appropriate quantity of the isotopically-labeled internal standard mixture (Standard Mixture A described earlier) to the aqueous liquid sample (or an aliquot thereof) in a screw-capped bottle fitted with a Teflon-lined cap. Add approximately 25% by volume of hexane to the spiked aqueous sample, seal the bottle and agitate on a shaker for a period of three hours. Allow the vessel to stand until the aqueous and organic layers separate, then transfer the organic layer to a separate sample bottle. Repeat the hexane extraction sequence two additional times and combine the organic fractions with that from the first extraction. Proceed with the sample fractionation and cleanup procedures described below.

6.3 Solid Samples

Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene and reflux for a period of one hour. Remove the toluene and discard it, retaining the silica gel, or if desired, retain a portion of the toluene to check for background contamination. For extraction of particulates, place the entire sample in the thimble onto the bed of precleaned silica gel (1 cm. thick), and top with the precleaned glass wool retained from the initial Soxhlet cleaning procedure. Add the appropriate quantity of the isotopically-labelled internal standard mixture (Standard Mixture A described earlier) to the sample in the Soxhlet thimble. Charge the Soxhlet with toluene and reflux for a period of 16 hours. After extraction, allow the Soxhlet to cool, remove the toluene extract, and transfer it to another sample vessel. Concentrate the extract to a volume of approximately 40 ml by using the nitrogen blowdown apparatus described earlier. Proceed with the sample fractionation and cleanup procedures described below.

7. Procedures for Cleanup and Fractionation of Sample Extracts

The following column chromatographic sample clean-up procedures are used in the order given, although not all may be required. In general, the silica and alumina column procedures are considered to be a minimum requirement. Acceptable alternative cleanup procedures may be used provided that they are demonstrated to effectively transmit a

representative set of the analytes of interest. The column chromatographic procedures listed here have been demonstrated to be effective for a mixture consisting of 1,2,3,4-TCDD, 2,3,7,8-TCDD, 2,3,6,8-TCDF, 1,2,4,8-TCDF, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD, 1,2,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDD, 1,2,4,6,7.9-HxCDF, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,8,9-HpCDF, OCDD and OCDF

An extract obtained as described in the foregoing sections is concentrated to a volume of about 1 mL using the nitrogen blowdown apparatus, and this is transferred quantitatively (with rinsings) to the combination silica gel column described below.

7.1 Combination Silica Gel Column: Pack one end of a glass column (20 mm. O.D. x 230 mm in length) with glass wool (precleaned) and add, in sequence, 1 g silica gel, 2 g base-modified silica gel, 1 g silica gel, 4 g acid-modified silica gel, and 1 g silica gel. (Silica gel and modified silica gel are prepared as described in the Reagents sections of this protocol.) Preelute the column with 30 mL hexane and discard the eluate. Add the sample extract in 5 mL of hexane to the column along with two additional 5 ml rinses. Elute the column with an additional 90 mL of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml.

7.2 Basic Alumina Column: Cut off a 10 mL disposable Pasteur glass pipette at the 4 mL graduation mark and pack the lower section with glass wool (precleaned) and 3 g of Woelm basic alumina (prepared as described in the Reagent section of this protocol). Transfer the concentrated extract from the combination silica column to the top of the column and elute the column sequentially with 15 mL of hexane, 10 mL of 8% methylene chloride-in-hexane and 15 mL of 50% methylene chloride-in-hexane, discarding the first two eluate fractions and retaining the third eluate fraction. Concentrate the latter fraction to about 0.5 mL using the nitrogen blowdown apparatus described earlier.

7.3 PX-21 Carbon/Celite 545 Column: Take a 9 inch disposable Pasteur pipette and cut off a 0.5 inch section from the constricted tip. Insert a filter paper disk at the top of the tube, 2.5 cm. from the constriction. Add a sufficient quantity of PX-21 Carbon/Celite 545 (Prepared as described in the reagent section of this protocol) to the tube to form a 2 cm. length of the Carbon-Celite. Insert a glass wool plug. Preelute the column in sequence with 2 mL of 50% benzene-in-ethyl acetate, 1 mL of 50% methylene chloride-in-cyclohexane and 2 mL of hexane, and discard these eluates. Load the extract (in 1 mL of hexane) from the alumina column onto the top of the column, along with 1 mL hexane rinse. Elute the column with 2 mL of 50% methylene chloride-in-hexane and 2 mL of 50% benzene-in-ethyl acetate and discard these eluates. Invert the column and reverse elute it with 4 mL of toluene, retaining this eluate. Concentrate the eluate and transfer it to a Reacti-Vial for storage. Store extracts in a freezer, shielded from light, prior

to GC-MS analysis. If desired, still another column chromatographic clean-up step can be employed prior to concentration of the extract, as described below.

7.4 Silica/Diol Micro Column Cleanup: After the above clean-up steps small amounts of highly colored polar compounds may be present in complex samples. These are removed, if necessary, by the following column: Push a small plug of glass wool into a disposable 6 mm i.d. glass Pasteur pipette, followed by 3 mm of Sepralyte (Analytichem International), 6 mm of silica gel and finally 3 mm of sodium sulfate. The column is pre-wet with hexane, the sample is applied in 100 µL of 100% hexane and eluted with hexane, collecting 1.5 ml.

8. Procedure for Analysis of Sample Extracts for PCDD/PCDF Using Gas Chromatography-Mass Spectrometry (GC-MS).

8.1 Sample extracts prepared by the procedures described in the foregoing are analyzed by GC-MS utilizing the following instrumental parameters. Typically, 1 to 5 µL portions of the extract are injected into the GC. Sample extracts are first analyzed using the DB-5 capillary GC column to obtain data on the concentrations of total tetra-through octa-CDDs and CDFs, and on 2,3,7,8-TCDD. If tetra-CDFs are detected in this analysis, then another aliquot of the sample is analyzed in a separate run, using the DB-225 column to obtain data on the concentration of 2,3,7,8-TCDF.

8.2 Gas Chromatograph

8.2.1 Injector: Configured for capillary column, splitless/split injection (split flow on 60 seconds following injection), injector temperature, 250°C.

8.2.2 Carrier gas: Hydrogen, 30 lb head pressure.

8.2.3 Capillary Column 1: For total tetra- through octa - CDDs/CDFs and 2,3,7,8-TCDD, 60 M x 0.25 mm I.D. fused silica DB-5; temperature programmed (see Table 1 for temperature program). Capillary Column 2: for 2,3,7,8-TCDF only, 60 M x 0.25 mm I.D. fused silica DB-225, temperature programmed (180°C for 1 min., then increase from 180°C to 240°C @ 5°C/min., hold at 240°C for 1 min.)

8.2.4 Interface Temperature: 250°C

8.3 Mass Spectrometer

8.3.1 Ionization Mode: Electron impact (70 eV)

8.3.2 Static Resolution: 1:600 (10% valley) or 1:10,000 depending upon requirements. Usually the sample extracts are initially analyzed using low resolution MS, then if PCDD/PCDF are detected, it is desirable to analyze a second portion of the sample extract using high resolution MS.

8.3.3 Source Temperature: 250°C

8.3.4 Ions Monitored: Computer-Controlled Selected-Ion Monitoring, See Table 1 for list of ion masses monitored and time intervals during which ions characteristic of each class of CDDs and CDFs are monitored.

8.4 Calibration Procedures:

8.4.1 Calibrating the MS Mass Scale: Perfluoro Kerosene, decafluorotriphenyl phosphine, or any other accepted mass marker compound must be introduced into the MS, in order to calibrate the mass scale through at least m/z 500. The procedures specified by the manufacturer for the particular MS instrument used are to be employed for this purpose. The mass calibration should be rechecked at least at 8 hr. operating intervals.

8.4.2 Table 1 shows the GC temperature program typically used to resolve each chlorinated class of PCDD and PCDF from the other chlorinated classes, and indicates the corresponding time intervals during which ions indicative of each chlorinated class are monitored by the MS. This temperature program and ion monitoring time cycle must be established by each analyst for the particular instrumentation used by injecting aliquots of Standard Mixtures C, D. and E (See earlier section of this protocol for description of these mixtures). It may be necessary to adjust the temperature program and ion monitoring cycles slightly based on the observations from analysis of these mixtures.

8.4.3 Checking GC Column Resolution for 2,3,7,8-TCDD and 2,3,7,8-TCDF: Utilize the column-resolution TCDD and TCDF isomer mixtures (Standard Mixtures D and E, containing 50 pg/µl, respectively of the appropriate TCDD and TCDF isomers) to verify that 2,3,7,8-TCDD and 2,3,7,8-TCDF are separated from the other TCDD and TCDF isomers, respectively. A 20% valley or less must be obtained between the mass chromatographic peak observed for 2,3,7,8-TCDD and adjacent peaks arising from other TCDD isomers, and similar separation of 2,3,7,8-TCDF from other neighboring TCDFs, is required. Standard Mixture D is utilized with the DB5 column and Standard Mixture E with the DB-225 column. Analyze the column performance standards using the instrumental parameters specified in Sections 8.2 and 8.3, and in Table 1. The column performance evaluation must be performed each time a new column is installed in the gas chromatograph, and at least once during each 8 hour operating period. Providing that the same column is employed for a

period of time, its performance can also be gauged by noting the peak width (at 1/2 peak height) for 2,3,7,8-TCDD or for 2,3,7,8-TCDF. If this peak width is observed to broaden by 20% or more as compared to the usual width for satisfactory operation, then the column resolution is suspect and must be checked. If the column resolution is found to be insufficient to resolve 2,3,7,8-TCDD and 2,3,7,8-TCDF from their neighboring TCDD and TCDF isomers, respectively, (as measured on the two different columns used for resolving these two isomers), then a new DB-5 and/or DB-225 GC column must be installed.

8.4.4 Calibration of the GC-MS-DS system to accomplish quantitative analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF, and of the total tetra- through octa-CDDs and CDFs contained in the sample extract, is accomplished by analyzing a series of at least three working calibration standards. Each of these standards is prepared to contain the same concentration of each of the stable-isotopically labelled internal standards used here (Standard Mixture A) but a different concentration of native PCDD/PCDF (Standard Mixture C). Typically, mixtures will be prepared so that the ratio of native PCDD and PCDF to isotopically-labelled PCDD and PCDF will be on the order of 0.1, 0.5 and 1.0 in the three working calibration mixtures. The actual concentrations of both native and isotopically-labelled PCDD and PCDF in the working calibration standards will be selected by the analyst on the basis of the concentrations to be measured in the actual sample extracts. At the time when aliquots of each of the standards are injected (and also when injecting aliquots of actual sample extracts), if desired, an aliquot of a standard containing typically 1 ng of $^{37}Cl_4$-2,3,7,8-TCDD (Standard B) can be drawn into the micro syringe containing the calibration solution described above (or the sample extract) and this is then co-injected along with the sample extract in order to obtain data permitting calculation of the percent recovery of the $^{13}C_{12}$-2,3,7,8-TCDD internal standard. Equations for calculating relative response factors from the calibration data derived from the calibration standard analyses, and for calculating the recovery of the $^{13}C_{12}$-2,3,7,8-TCDD and the other isotopically-labelled PCDD and PCDF, and the concentration of native PCDD and PCDF in the sample (from the extract analysis), are summarized below. In these calculations, as can be seen, 2,3,7,8-TCDD is employed as the illustrative model. However, the calculations for each of the other native dioxins and furans in the sample analyzed are accomplished in an analgous manner. It should be noted that in view of the fact that stable-isotopically labelled internal standards corresponding to each tetra- through octachlorinated class are not used here (owing to limited availability at this time) the following approach is adopted: For quantitation of tetrachlorinated dibenzofurans $^{13}C_{12}$-2,3,7,8-TCDF is used as the internal standard. For quantitation of tetrachloro-dibenzo-p-dioxins, $^{13}C_{12}$-2,3,7,8-TCDD is used as the internal standard. For quantitation of PeCDD, HxCDD, PeCDF, and HxCDF, the corresponding stable-isotopically labelled HxCDD and HxCDF internal standards are used. For quantitation of HpCDD, OCDD, and HpCDF, OCDF, the isotopically-labelled OCDD and OCDF, respectively, are used. Inherent in this approach is the assumption that the response factors for each of the isomers

of each chlorinated class are the same, and in the case of the penta- and hepta-CDDs and CDFs, the assumption is made that the responses for these two classes are equivalent to those for the tetra-isomers and the octa-isomers, respectively.

8.4.5 Equations for Calculating Response Factors, Concentration of 2,3,7,8-TCDD In An Unknown Sample, and Recoveries of Internal Standards.

Equation 1: Response Factor (RRF) for native 2,3,7,8-TCDD using $^{13}C_{12}$-2,3,7,8-TCDD as an internal standard.

$$RRF_d = (A_s C_{is} / A_{is} C_s)$$

where: A_s = SIM response for 2,3,7,8-TCDD ion at m/z 320 + 322

A_{is} = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

C_{is} = Concentration of the internal standard (pg./µL.)

C_s = Concentration of the 2,3,7,8-TCDD (pg./µL.)

Equation 2: Response Factor (RRF) for $^{37}Cl_4$-2,3,7,8-TCDD, the co-injected external standard

$$RRF_f = (A_{is} C_{es}) / (A_{es} C_{is})$$

where: A_{is} = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

A_{es} = SIM response for co-injected $^{37}Cl_4$-2,3,7,8-TCDD external standard at m/z 328 - 0.009 (SIM response for native 2,3,7,8-TCDD at m/z 322)

C_{is} = Concentration of the internal standard (pg./µL.)

C_{es} = Concentration of the external standard (pg./µL.)

Equation 3: Calculation of concentration of native 2,3,7,8-TCDD using $^{13}C_{12}$-2,3,7,8-TCDD as internal standard

$$\text{Concentration, pg./g.} = (A_s)\ (I_s)/(A_{is})(RRF_d)(W)$$

where: A_s = SIM response for 2,3,7,8-TCDD ion at m/z 320 + 322

A_{is} = SIM response for the $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

I_s = Amount of internal standard added to each sample (pg.)

W = Weight of soil or waste in grams

RRF_d = Relative response factor from Equation 1

Equation 4: Calculation of % recovery of $^{13}C_{12}$-2,3,7,8-TCDD internal standard

$$\% \text{ Recovery} = 100(A_{is})(E_s)/(A_{es})(I_i)(RRF_f)$$

A_{is} = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

A_{es} = SIM response for $^{37}Cl_4$-2,3,7,8-TCDD external standard ion at m/z 328 - 0.009 (SIM Response for native 2,3,7,8-TCDD at m/z 322)

E_s = Amount of $^{37}Cl_4$-2,3,7,8-TCDD external standard co-injected with sample extract (ng.)

I_i = Theoretical amount of $^{13}C_{12}$-2,3,7,8-TCDD internal standard in injection

RRF_f = Relative response factor from Equation 2

As noted above, procedures similar to these are applied to calculate analytical results for all of the other PCDD/PCDF determined in this method.

8.5 Criteria Which GC-MS Data Must Satisfy for Identification of PCDD/PCDF in Samples Analyzed and Additional Details of Calculation Procedures.

In order to identify specific PCDD/PCDF in samples analyzed, the GC-MS data obtained must satisfy the following criteria:

8.5.1 Mass spectral responses must be observed at both the molecular and fragment ion masses corresponding to the ions indicative of each chlorinated class of PCDD/PCDF identified (see Table 1) and intensities of these ions must maximize essentially simultaneously (within $\pm$ 1 second). In addition, the chromatographic retention times observed for each PCDD/PCDF signal must be correct relative to the appropriate

stable-isotopically labelled internal standard and must be consistent with the retention time windows established for the chlorinated group to which the particular PCDD/PCDF is assigned.

8.5.2 The ratio of the intensity of the molecular ion $(M)^+$ signal to that of the $(M+2)^+$ signal must be within $\pm$ 10% of the theoretically expected ratio (for example, 0.77 in the case of TCDD; therefore the acceptable range for this ratio is 0.62 to 0.92).

8.5.3 The intensities of the ion signals are considered to be detectable if each exceeds the baseline noise by a factor of at least 3:1. The ion intensities are considered to be quantitatively measurable if each ion intensity exceeds the baseline noise by a factor of at least 5:1[c].

8.5.4 For reliable detection and quantitation of PCDF it is also desirable to monitor signals arising from chlorinated diphenyl ethers which, if present could give rise to fragment ions yielding ion masses identical to those monitored as indicators of the PCDF. Accordingly, in Table 1, appropriate chlorinated diphenyl ether masses are specified which must be monitored simultaneously with the PCDF ion-masses. Only when the response for the diphenyl ether ion mass is not detected at the same time as the PCDF ion mass can the signal obtained for an apparent PCDF be considered unique.

8.5.5 Measurement of the concentration of the congeners in a chlorinated class using the methods described herein is based on the assumption that all of the congeners are identical to the calibration standards employed in terms of their respective chemical and separation properties and in terms of their respective gas chromatographic and mass spectrometric responses. Using these assumptions, for example, the $^{13}C_{12}$-2,3,7,8-TCDD internal standard is utilized as the internal calibration standard for all of the 22 TCDD isomers or congeners. Furthermore, the concentration of the total TCDD present in a sample extract is determined by calculating, on the basis of the standard procedure outlined above, the concentration of each TCDD isomer peak (or peaks for multiple TCDD isomers, where these coelute) and these individual concentrations are subsequently summed to obtain the concentration of "total" TCDD.

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c. In practice, the analyst can estimate the baseline noise by measuring the extension of the baseline immediately prior to each of the two mass chromatographic peaks attributed to a given PCDD or PCDF. Spurious signals may arise either from electronic noise or from other organic compounds in the extract. Since it may be desirable to evaluate the judgement of the analyst in this respect, copies of original mass chromatograms must be included in the report of analytical results.

8.6 Frequently, during the analysis of actual sample extracts, extraneous compounds which are present in the extract (those organic compounds not completely removed during the clean-up phase of the analysis) can cause changes in the liquid and gas chromatographic elution characteristics of the PCDD/PCDF (typically retention times for the PCDD/PCDF are prolonged). Such extraneous organic compounds, when introduced into the mass spectrometer source may also result in a decrease in the sensitivity of the MS because of suppression of ionization, and other affects such as charge transfer phenomena. The shifts in chromatographic retention times are usually general shifts, that is, the relative retention times for the PCDD/PCDF are not changed, although the entire elution time scale is prolonged. The analyst's intervention in the GC-MS operating sequence can correct for the lengthened GC retention times which are sometimes observed due to the presence of extraneous organics in the sample extract. For example, using the program outlined in Table 1, if the retention time observed for 2,3,7,8-TCDD (which normally is 19.5 minutes) is lengthened by 30 seconds or more, appropriate adjustments in the programming sequence outlined in Table 1 can be made, that is, each selected ion-monitoring program is delayed by a length of time proportionate to the lengthening of the retention time for the 2,3,7,8-TCDD isomer. In the case of ionization suppression, this phenomenon is inherently counteracted by the internal standard approach. However, if loss of sensitivity due to ionization suppression is severe, additional clean-up of the sample extract may be required in order to achieve the desired detection limits.

9. Quality Assurance/Quality Control

9.1 Quality assurance and quality control are ensured by the following provisions:

9.1.1 Each sample analyzed is spiked with stable isotopically labelled internal standards, prior to extraction and analysis. Recoveries obtained for each of these standards should typically be in the range from 60-90%. Since these compounds are used as true internal standards however, lower recoveries do not necessarily invalidate the analytical results for native PCDD/PCDF, but may result in higher detection limits than are desired.

9.1.2 Processing and analysis of at least one method blank sample is accomplished for each set of samples (a set being defined as 20 samples or less).

9.1.3 It is desirable to analyze at least one sample spiked with representative native PCDD/PCDF for each set of 20 or fewer samples. The result of this analysis provides an indication of the efficacy of the entire analytical procedure. The results of this analysis will be considered acceptable if the detected concentration of each of the native

PCDD/PCDF added to the sample is within ±50% of the known concentration. (An appropriate set of native isomers to be added here is a set such as that indicated for Standard Mixture C.)

9.1.4 At least one of the samples analyzed out of each set (of 20 samples or less) is analyzed in duplicate and the results of the duplicate analysis are included in the report of data.

9.1.5 Performance evaluation samples prepared by EPA, or other laboratories, which contain representative PCDD/PCDF in concentrations approximating those present in typical field samples being analyzed (but unknown to the analyzing lab) should be periodically distributed to laboratories accomplishing these analyses.

9.1.6 Sources of all calibration and performance standards used in the analyses and the purity of these materials must be specified in the data report.

10. Data Reporting

10.1 Each report of analyses accomplished using the protocol described herein will typically include tables of results which include the following:

10.1.1 Complete identification of the samples analyzed (sample numbers and source).

10.1.2 The dates and times at which all analyses were accomplished. This information should also appear on each mass chromatogram included with the report.

10.1.3 Raw mass chromatographic data which consists of the absolute intensities (based on either peak height or peak area) of the signals observed for the ion-masses monitored (See Table 1).

10.1.4 The calculated ratios of the intensities of the molecular ions for all PCDD/PCDF detected.

10.1.5 The calculated concentrations of native 2,3,7,8-TCDD and 2,3,7,8-TCDF, and the total concentrations of the congeners of each class of PCDD/PCDF for each sample analyzed, expressed in nanograms TCDD per gram of sample (that is, parts-per-billion) as determined from the raw data. If no PCDD/PCDF are detected, the notation "Not Detected" or "N.D." is used, and the minimum detectable concentrations

(or detection limits) are reported.

10.1.6 The same raw and calculated data which are provided for the actual samples will also be reported for the duplicate analyses, the method blank analyses, the spiked sample analyses and any other QA or performance samples analyzed in conjunction with the actual sample set(s).

10.1.7 The recoveries of the internal standards in percent.

10.1.8 The recoveries of the native PCDD/PCDF from spiked samples in percent.

10.1.9 The calibration data, including response factors calculated from the three point calibration procedure described elsewhere in this protocol. Data showing that these factors have been verified at least once during each 8 hour period of operation or with each separate set of samples analyzed must be included.

10.1.10 The weight or quantity of the original sample analyzed.

10.1.11 Documentation of the source of all PCDD/PCDF standards used and available specifications on purity.

10.1.12 In addition to the tables described above, each report of analyses will include all mass chromatograms obtained for all samples analyzed, as well as for all calibration, GC column performance, and GC "window" definition runs and results of column performance checks.

10.1.13 Any deviations from the procedures described in this protocal which are applied in the analyses of samples will be documented in detail in the analytical report.

11. Typical Data Indicative of Method Performance - Precision and Accuracy.

11.1 The method described herein has typically been employed to quantitatively determine 2,3,7,8-TCDD in combustion product samples at concentrations as low as 10 picograms/gram and as high at 100 µg/g. Concentrations of the other PCDD/PCDF which can be detected typically fall within the range of 20 picograms/isomer/gram of sample, to 100 picograms/g of sample. Of course, the limits of detection which can be practically achieved are dependent on the quantity of sample available

and the amount and kind of other interferring organic residues which are present in the sample. With respect to precision, the average deviation of data obtained from the analyses of a number of aliquots of the same sample containing the 2,3,7,8-TCDD isomer in the 250-300 ppb range is estimated to be ±10% or better. Data on the precision of quantitation of multiple PCDD/PCDF in a single sample are not as yet available. As yet, there is inadequate interlaboratory and performance evaluation data available to specify the accuracy which can be expected of the analytical procedures described herein.

TABLE 1. Sequence of Operations in GC-MS-DS Quantitation of CDDs/CDFs in Extracts of Environmental Samples

Elapsed Time (min)	Event	GC Column Temperature* (°C)	Temperature Program Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approximate Theoretical Ratio of $[M]^+$:$[M+2]^+$
0.00	Injection, splitless	190					
1.00	Turn on split valve	190					
1.00	Begin temp. program to 220°C	190	5				
6.00	Open column flow to mass spectrometer	215	5				
7.00	Column temperature hold	220					
14.00	Start Tetra Program; sweep = 350 ppm; time/mass = 0.08 sec.			240.938	$[M-COCl]^+$	TCDF	
				258.930	$[M-COCl]^+$	TCDD	
				303.902	$[M]^+$	TCDF	0.77
				305.899	$[M+2]^+$	TCDF	
				315.942	$[M]^+$	$^{13}C_{12}$-TCDF	
				319.897	$[M]^+$	TCDD	0.77
				321.894	$[M+2]^+$	TCDD	
				327.885	$[M]^+$	$^{37}Cl_4$-TCDD	
				331.937	$[M]^+$	$^{13}C_{12}$-TCDD	
				373.840	$[M]^+$	HxDPE[a].	
22.00	Stop Tetra Program	220					
22.50	Start Penta Program; sweep = 350 ppm; time/mass = 0.12 sec.			274.899	$[M-COCl]^+$	PeCDF	
				290.894	$[M-COCl]^+$	PeCDD	
				337.863	$[M]^+$	PeCDF	0.61
23.00	Begin temp. program to 235°	220	5	339.860	$[M+2]^+$	PeCDF	
26.00	Column temperature hold	235		353.858	$[M]^+$	PeCDD	0.61
				355.855	$[M+2]^+$	PeCDD	
				407.801	$[M]^+$	HpDPE[a].	
32.00	Stop Penta Program						
32.50	Start Hexa Program; sweep = 350 ppm; time/mass = 0.20 sec.	235		310.857	$[M-COCl]^+$	HxCDF	
				326.852	$[M-COCl]^+$	HxCDD	
				373.821	$[M]^+$	HxCDF	1.23
				375.821	$[M+2]^+$	HxCDF	
				385.861	$[M]^+$	$^{13}C_{12}$-HxCDF	
				389.816	$[M]^+$	HxCDD	1.23
				391.813	$[M+2]^+$	HxCDD	
				411.856	$[M]^+$	$^{13}C_{12}$-HxCDD	
				443.759	$[M]^+$	ODPE[a].	

TABLE 1. Sequence of Operations in GC-MS-DS Quantitation of CDDs/CDFs in Extracts of Environmental Samples (Cont.)

Elapsed Time (min)	Event	GC Column Temperature (°C)	Temperature Program Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approximate Theoretical Ratio of $[M]^+$:$[M+2]^+$
33.00	Begin temp. program to 250°C	235	5				
36.00	Column temperature hold	250					
42.50	Stop Hexa Program						
43.00	Start Hepta Program; sweep = 350 ppm; time/mass = 0.30 sec.	250		344.818	$[M-COCl]^+$	HpCDF	
				360.813	$[M-COCl]^+$	HpCDD	
				407.782	$[M]^+$	HpCDF	1.03
				409.779	$[M+2]^+$	HpCDF	
				423.777	$[M]^+$	HpCDD	1.03
				425.774	$[M+2]^+$	HpCDD	
				477.720	$[M^+]$	NDPE[a].	
53.00	Stop Hepta Program	250					
53.50	Start Octa Program; sweep = 350 ppm; time/mass = 0.30 sec.	250		378.768	$[M-COCl]^+$	OCDF	
				394.774	$[M-COCl]^+$	OCDD	
				441.732	$[M]^+$	OCDF	0.88
54.00	Begin temp. program to 270°	250°	5	443.740	$[M+2]^+$	OCDF	
58.00	Column temperature hold	270°		453.772	$[M]^+$	$^{13}C_{12}$-OCDF	
				457.738	$[M]^+$	OCDD	0.88
				459.735	$[M+2]^+$	OCDD	
				469.779	$[M]^+$	$^{13}C_{12}$-OCDD	
				471.776	$[M+2]^+$	$^{13}C_{12}$-OCDD	
				511.681	$[M]^+$	DDPE[a].	
65.00	Stop Octa Program						
65.00	Begin temp. program to 300°	270°	5				
71.00	Column temperature hold	300°					
75.00	Cool Column to 190°						

[a] HxDFE, HpDPE, ODPE, NDPE, DDPE are abbreviations which designate (respectively) hexachloro-, heptachloro-, octachloro-, nonachloro-, and decachlorodiphenyl ethers.

*The parameters given here are applicable for a 60-meter fused silica capillary GC column coated with DB-5.